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(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 957 474 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

17.11.1999 Bulletin 1999/46

(51) Int Cl.⁶: **G11B 5/72, G11B 5/712,
C09C 3/12**

(21) Application number: **99303761.3**

(22) Date of filing: **14.05.1999**

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: **15.05.1998 JP 15216298**

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(54) **Magnetic recording medium**

(57) A magnetic recording medium comprising:

(a) a non-magnetic base film; and

(b) a magnetic recording layer comprising a binder resin and black magnetic acicular composite particles which have an average particle diameter of 0.051 to 0.72 μm and which comprise:

- magnetic acicular particles,
- a coating on the surface of said magnetic acicular particles, comprising at least one organosilicon compound selected from:

(1) organosilane compounds obtainable by drying or heat-treating alkoxysilane compounds,

(2) polysiloxanes or modified polysiloxanes, and

(3) fluoroalkyl organosilane compounds obtainable by drying or heat-treating fluoroalkylsilane compounds, and

- from 0.5 to 10 parts by weight, per 100 parts by weight of said magnetic acicular particles, of carbon black particles which have a particle size of 0.002 to 0.05 μm and which are adhered to said coating.

Description

[0001] The present invention relates to a magnetic recording medium, and more particularly, to a magnetic recording medium capable of not only showing a low light transmittance and a low surface resistivity even when the amount of carbon black fine particles added to a magnetic recording layer thereof is as small as possible, but also having a smooth surface by using therein black magnetic acicular composite particles which are excellent in dispersibility in a vehicle due to less amount of carbon black fine particles fallen-off from the surface of each black magnetic acicular composite particle, and have a high blackness and a low volume resistivity.

[0002] With a development of miniaturized, lightweight video or audio magnetic recording and reproducing apparatuses for long-time recording, magnetic recording media such as a magnetic tape and magnetic disk have been increasingly and strongly desired to have a higher performance, namely, a higher recording density, higher output characteristic, in particular, an improved frequency characteristic and a lower noise level.

[0003] Especially, video tapes have recently been desired more and more to have a higher picture quality, and the frequencies of carrier signals recorded in recent video tapes are higher than those recorded in conventional video tapes. In other words, the signals in the short-wave region have come to be used, and as a result, the magnetization depth from the surface of a magnetic tape has come to be remarkably small.

[0004] In order to enhance output characteristics of magnetic recording media, especially an S/N ratio thereof with respect to signals having a short wavelength, there have been demanded fineness of magnetic particles, reduction in thickness of a magnetic recording layer, high dispersibility of magnetic particles and surface smoothness of a magnetic coating film.

[0005] On the other hand, at the present time, the end position of a magnetic recording medium such as magnetic tapes has been detected by sensing a high light transmittance portion of the magnetic recording medium by means of a video deck. In the case where the particle size of magnetic particles dispersed in the magnetic recording layer become finer and the thickness of the magnetic recording medium is reduced in order to meet the requirement for high performance of the magnetic recording medium as described hereinbefore, the magnetic recording medium shows a high light transmittance as a whole, so that it has been difficult to detect the end position thereof by means of the video deck. In order to solve this problem, carbon black fine particles have been added to the magnetic recording layer in an amount of usually about 6 to 12 parts by weight based on 100 parts by weight of the magnetic particles, thereby reducing the light transmittance of the magnetic recording medium. For this reason, in current videotapes, it is essential to add carbon black fine particles, etc., to the magnetic recording layer thereof.

[0006] However, when a large amount of such non-magnetic carbon black fine particles are added to the magnetic recording layer, the magnetic recording medium suffers from deterioration in signal recording property, thereby hindering high-density recording thereon, and the reduction in thickness of the magnetic recording layer becomes incapable. Further, due to the fact that the carbon black fine particles have an average particle size as fine as 0.002 to 0.05 μm and a large BET specific surface area value, and are deteriorated in solvent-wettability, it has been difficult to disperse these carbon black fine particles in vehicle, thereby failing to obtain a magnetic recording medium having a smooth surface.

[0007] Therefore, it has been strongly demanded to provide a magnetic recording medium having a sufficiently low light transmittance even when the amount of carbon black fine particles added to the magnetic recording layer is as small as possible, especially when the carbon black fine particles is used in an amount as small as less than 6 parts by weight based on 100 parts by weight of magnetic particles.

[0008] Further, in the case where the magnetic recording medium has a high surface resistivity, the electrostatic charge amount thereof is increased, so that cut chips or dusts tend to adhere onto the surface of the magnetic recording medium upon the production or use thereof, thereby causing such a problem that the dropout frequently occurs. Therefore, in order to reduce not only the light transmittance of the magnetic recording medium but also the surface resistivity thereof, especially below about $10^{10} \Omega/\text{sq}$, the carbon black fine particles have been conventionally added to the magnetic recording layer of the magnetic recording medium.

[0009] However, as described above, in the case where the amount of such carbon black fine particles or the like which do not contribute to magnetic properties of the magnetic recording layer, is increased, there are caused such problems that the magnetic recording medium suffers from deterioration in signal recording property, the reduction in thickness of the magnetic recording layer becomes incapable, and further the surface smoothness of the magnetic recording layer is deteriorated.

[0010] Also, since the carbon black fine particles are bulky particles having a bulk density as low as about 0.1 g/cm³, the handling property and workability thereof are deteriorated. In addition, it has been pointed out that the use of such carbon black fine particles causes problems concerning safety and hygiene such as carcinogenesis.

[0011] As the conventional method of reducing the light transmittance and surface resistivity of the magnetic recording medium by lessening the amount of carbon black fine particles added to the magnetic recording layer, there is known a method of increasing the blackness of magnetic particles themselves by incorporating Fe²⁺ into magnetic acicular

cobalt-coated iron oxide particles in an amount of not less than 6.0 % by weight based on the weight of the magnetic acicular cobalt-coated iron oxide particles (Japanese Patent Application Laid-Open (KOKAI) No. 3-102617(1991) or the like).

[0012] However, at present, although it has been most strongly demanded to provide a magnetic recording medium capable of not only showing a low light transmittance and a low surface resistivity even when the amount of carbon black fine particles added to the magnetic recording layer thereof is as small as possible, but also having a smooth surface, such magnetic recording medium which is capable of satisfying all of these properties, cannot be obtained yet.

[0013] That is, in the case of the known magnetic recording medium of Japanese Patent Application Laid-Open (KOKAI) No. 3-102617(1991) in which the magnetic acicular cobalt-coated iron oxide particles containing Fe^{2+} in the magnetic particles in an amount of not less than 6.0 % by weight are used as magnetic particles, the blackness of the magnetic particles is still unsatisfactory, so that the magnetic recording medium can show neither a sufficiently low light transmittance nor a sufficiently low surface resistivity as described in Comparative Examples hereinafter. Further, since the magnetic particles are deteriorated in dispersibility in vehicle due to the inclusion of Fe^{2+} , it has been difficult to obtain a magnetic recording layer having a smooth surface.

[0014] As a result of the present inventor's earnest studies, it has been found that by using as magnetic particles of a magnetic recording medium,

black magnetic acicular composite particles having an average particle diameter of 0.051 to 0.72 μm , comprising magnetic acicular particles,

a coating formed on surface of the magnetic acicular particles, comprising at least one organosilicon compound selected from the group consisting of:

- (1) organosilane compounds obtained by drying or heat-treating an alkoxysilane compounds,
- (2) polysiloxanes or modified polysiloxanes, and
- (3) fluoroalkyl organosilane compounds obtained by drying or heat-treating fluoroalkylsilane compounds, and

carbon black fine particles adhered on the coating, having a particle size of 0.002 to 0.05 μm , wherein the amount of the carbon black fine particles adhered is 0.5 to 10 parts by weight based on 100 parts by weight of the magnetic acicular particles,

the obtained magnetic recording medium can show a low light transmittance and a low surface resistivity, can have a smooth surface due to the fact that the amount of carbon black fine particles added to the magnetic recording layer can be lessened and the dispersibility of the black magnetic acicular particles themselves in vehicle can be enhanced, and, therefore, can be suitably used as magnetic recording media for high-density recording. The present invention has been attained on the basis of the finding.

[0015] It is an object of the present invention to provide a magnetic recording medium capable of not only showing a low light transmittance and a low surface resistivity even when the amount of carbon black fine particles added to a magnetic recording layer thereof is as small as possible, but also having a smooth surface.

[0016] To accomplish the aims, in a first aspect of the present invention, there are provided a magnetic recording medium comprising:

a non-magnetic base film; and

a magnetic recording layer comprising a binder resin and black magnetic acicular composite particles having an average particle diameter of 0.051 to 0.72 μm , comprising

magnetic acicular particles,

a coating formed on surface of the magnetic acicular particles, comprising at least one organosilicon compound selected from the group consisting of:

- (1) organosilane compounds obtained by drying or heat-treating an alkoxysilane compounds,
- (2) polysiloxanes or modified polysiloxanes, and
- (3) fluoroalkyl organosilane compounds obtained by drying or heat-treating a fluoroalkylsilane compounds, and

carbon black fine particles adhered on the coating, having a particle size of 0.002 to 0.05 μm ,

the amount of the carbon black fine particles adhered being 0.5 to 10 parts by weight based on 100 parts by weight of the magnetic acicular particles.

[0017] In a second aspect of the present invention, there are a magnetic recording medium comprising:

a non-magnetic base film; and

a magnetic recording layer comprising a binder resin and black magnetic acicular composite particles having an average particle diameter of 0.051 to 0.72 μm , comprising

magnetic acicular particles having a coat formed on at least a part of the surface of the magnetic acicular particle, comprising at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon in amount of 0.01 to 20 % by weight, calculated as Al or SiO_2 , based on the weight of the magnetic acicular particles,

a coating formed on surface of the magnetic acicular particles, comprising at least one organosilicon compound selected from the group consisting of:

- (1) organosilane compounds obtained by drying or heat-treating an alkoxysilane compounds,
- (2) polysiloxanes or modified polysiloxanes, and
- (3) fluoroalkyl organosilane compounds obtained by drying or heat-treating a fluoroalkylsilane compounds, and

carbon black fine particles adhered on the coating, having a particle size of 0.002 to 0.05 μm ,

the amount of the carbon black fine particles adhered being 0.5 to 10 parts by weight based on 100 parts by weight of the magnetic acicular particles.

[0018] In a third aspect of the present invention, there are provided black magnetic acicular composite particles for a magnetic recording medium, the black magnetic acicular composite particles having an average particle diameter of 0.051 to 0.72 μm , comprising:

magnetic acicular particles such as magnetic acicular iron oxide particles containing Co, Al, Ni, P, Zn, Si or B, magnetic acicular iron oxide particles coated with cobalt or cobalt and iron, or magnetic acicular metal particles containing iron as a main component,

a coating formed on surface of the magnetic acicular particles, comprising at least one organosilicon compound selected from the group consisting of:

- (1) organosilane compounds obtained by drying or heat-treating an alkoxysilane compounds,
- (2) polysiloxanes or modified polysiloxanes, and
- (3) fluoroalkyl organosilane compounds obtained by drying or heat-treating a fluoroalkylsilane compounds, and

carbon black fine particles adhered on the coating, having a particle size of 0.002 to 0.05 μm ,

the amount of the carbon black fine particles adhered being 0.5 to 10 parts by weight based on 100 parts by weight of the magnetic acicular particles.

[0019] In a fourth aspect of the present invention, there are provided black magnetic acicular composite particles for a magnetic recording medium, the black magnetic acicular composite particles having an average particle diameter of 0.051 to 0.72 μm , comprising:

magnetic acicular particles such as magnetic acicular iron oxide particles containing Co, Al, Ni, P, Zn, Si or B, magnetic acicular iron oxide particles coated with cobalt or cobalt and iron, or magnetic acicular metal particles containing iron as a main component, wherein the magnetic acicular particles have a coat formed on at least a part of the surface of the magnetic acicular particle, comprising at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon in amount of 0.01 to 20 % by weight, calculated as Al or SiO_2 , based on the weight of the magnetic acicular particles coated, a coating formed on surface of the magnetic acicular particles, comprising at least one organosilicon compound selected from the group consisting of:

- (1) organosilane compounds obtained by drying or heat-treating an alkoxysilane compounds,
- (2) polysiloxanes or modified polysiloxanes, and
- (3) fluoroalkyl organosilane compounds obtained by drying or heat-treating a fluoroalkylsilane compounds, and

carbon black fine particles adhered on the coating, having a particle size of 0.002 to 0.05 μm ,

the amount of the carbon black fine particles adhered being 0.5 to 10 parts by weight based on 100 parts by weight of the magnetic acicular particles.

[0020] In a fifth aspect of the present invention, there are provided a method of forming a magnetic recording medium

comprising a non-magnetic base film, and a magnetic recording layer comprising a binder resin and as magnetic particles black magnetic acicular composite particles having an average particle diameter of 0.051 to 0.72 μm , comprising

5 magnetic acicular particles,

a coating formed on surface of the magnetic acicular particles, comprising at least one organosilicon compound selected from the group consisting of:

- (1) organosilane compounds obtained by drying or heat-treating an alkoxysilane compounds,
- (2) polysiloxanes or modified polysiloxanes, and
- (3) fluoroalkyl organosilane compounds obtained by drying or heat-treating a fluoroalkylsilane compounds, and

carbon black fine particles adhered on the coating, having a particle size of 0.002 to 0.05 μm ,

the amount of the carbon black fine particles adhered being 0.5 to 10 parts by weight based on 100 parts by weight of the magnetic acicular particles.

[0021] In a sixth aspect of the present invention, there are provided a method of forming a magnetic recording medium comprising a non-magnetic base film, and a magnetic recording layer comprising a binder resin and as magnetic particles black magnetic acicular composite particles having an average particle diameter of 0.051 to 0.72 μm , comprising

magnetic acicular particles having a coat formed on at least a part of the surface of the magnetic acicular particle, comprising at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon in amount of 0.01 to 20 % by weight, calculated as Al or SiO_2 , based on the weight of the magnetic acicular particles coated,

a coating formed on surface of the magnetic acicular particles, comprising at least one organosilicon compound selected from the group consisting of:

- (1) organosilane compounds obtained by drying or heat-treating an alkoxysilane compounds,
- (2) polysiloxanes or modified polysiloxanes, and
- (3) fluoroalkyl organosilane compounds obtained by drying or heat-treating a fluoroalkylsilane compounds, and

carbon black fine particles adhered on the coating, having a particle size of 0.002 to 0.05 μm ,

the amount of the carbon black fine particles adhered being 0.5 to 10 parts by weight based on 100 parts by weight of the magnetic acicular particles.

[0022] In the accompanying drawings:

[0023] Fig. 1 is an electron micrograph (x 30,000) showing a particle structure of acicular cobalt-coated magnetite particles used in Example 1.

[0024] Fig. 2 is an electron micrograph (x 30,000) showing a particle structure of carbon black fine particles used in Example 1.

[0025] Fig. 3 is an electron micrograph (x 30,000) showing a particle structure of black magnetic acicular composite particles obtained in Example 1.

[0026] Fig. 4 is an electron micrograph (x 30,000) showing a particle structure of mixed particles composed of the acicular cobalt-coated magnetite particles and the carbon black fine particles, for comparative purpose.

[0027] Fig. 5 is an electron micrograph (x 30,000) showing a particle structure of surface-treated spindle-shaped cobalt-coated maghemite particles obtained in "Core particles 7".

[0028] Fig. 6 is an electron micrograph (x 30,000) showing a particle structure of black magnetic spindle-shaped composite particles obtained in Example 10.

[0029] Fig. 7 is an electron micrograph (x 30,000) showing a particle structure of mixed particles composed of the surface-treated spindle-shaped cobalt-coated maghemite particles and the carbon black fine particles, for comparative purpose.

[0030] The present invention is explained in more detail below.

[0031] First, black magnetic acicular composite particles for a magnetic recording layer of a magnetic recording medium according to the present invention are described.

[0032] The black magnetic acicular composite particles having an average particle diameter of 0.051 to 0.72 μm according to the present invention, comprise magnetic acicular particle as a core particle, a coating comprising an organosilicon compound which is formed on the surface of each magnetic acicular particle, and carbon black fine

particles having an average particle size of 0.002 to 0.05 μm , which are adhered on the coating comprising the organosilicon compound.

[0033] As the magnetic acicular particles used as core particles in the present invention, there may be exemplified magnetic acicular iron oxide particles such as acicular magnetite particles (Fe_3O_4), acicular maghemite particles ($\gamma\text{-Fe}_2\text{O}_3$), acicular berthollide compounds particles ($\text{FeO}_x \cdot \text{Fe}_2\text{O}_3$; $0 < x < 1$) which are intermediate oxides between maghemite and magnetite; magnetic acicular iron oxide particles obtained by incorporating different kinds of elements other than Fe such as Co, Al, Ni, P, Zn, Si or B into the above-mentioned magnetic acicular iron oxide particles; magnetic acicular coated iron oxide particles obtained by coating the surface of the above-mentioned magnetic acicular iron oxide particles or those containing different kinds of elements, with cobalt, both cobalt and iron or the like (hereinafter referred to merely as "magnetic acicular cobalt-coated iron oxide particles"); magnetic acicular metal particles containing iron as a main component which contain elements other than Fe such as Co, Al, Ni, P, Zn, Si, B or rare earth elements (hereinafter referred to merely as "magnetic acicular metal particles") (which may include magnetic acicular iron alloy particles containing elements other than Fe such as Co, Al, Ni, P, Zn, Si, B or rare earth elements); or the like.

[0034] Under the consideration of oxidation stability and dispersibility, the magnetic acicular cobalt-coated iron oxide particles are preferred. The amount of the cobalt coated on the surface of the acicular iron oxide particle as a core particle is preferably 0.5 to 10 % by weight based on the weight of the magnetic acicular cobalt-coated iron oxide particles.

[0035] Under the consideration of high-density recording of recent magnetic recording media, as the magnetic acicular particles, the magnetic acicular cobalt-coated iron oxide particles, and the magnetic acicular metal particles are preferred. Among them, the magnetic acicular metal particles are more preferred.

[0036] More specifically, the magnetic acicular metal particles may be exemplified as follows.

1) Magnetic acicular metal particles comprises iron; and cobalt of usually 0.05 to 40 % by weight, preferably 1.0 to 35 % by weight, more preferably 3 to 30 % by weight (calculated as Co) based on the weight of the magnetic acicular metal particles.

2) Magnetic acicular metal particles comprises iron; and aluminum of usually 0.05 to 10 % by weight, preferably 0.1 to 7 % by weight (calculated as Al) based on the weight of the magnetic acicular metal particles.

3) Magnetic acicular metal particles comprises iron; cobalt of usually 0.05 to 40 % by weight, preferably 1.0 to 35 % by weight, more preferably 3 to 30 % by weight (calculated as Co) based on the weight of the magnetic acicular metal particles; and aluminum of usually 0.05 to 10 % by weight, preferably 0.1 to 7 % by weight (calculated as Al) based on the weight of the magnetic acicular metal particles.

4) Magnetic acicular metal particles comprises iron; cobalt of usually 0.05 to 40 % by weight, preferably 1.0 to 35 % by weight, more preferably 3 to 30 % by weight (calculated as Co) based on the weight of the magnetic acicular metal particles; and at least one selected from the group consisting of Nd, La and Y of usually 0.05 to 10 % by weight, preferably 0.1 to 7 % by weight (calculated as the corresponding element) based on the weight of the magnetic acicular metal particles.

5) Magnetic acicular metal particles comprises iron; aluminum of usually 0.05 to 10 % by weight, preferably 0.1 to 7 % by weight (calculated as Al) based on the weight of the magnetic acicular metal particles; and at least one selected from the group consisting of Nd, La and Y of usually 0.05 to 10 % by weight, preferably 0.1 to 7 % by weight (calculated as the corresponding element) based on the weight of the magnetic acicular metal particles.

6) Magnetic acicular metal particles comprises iron; cobalt of usually 0.05 to 40 % by weight, preferably 1.0 to 35 % by weight, more preferably 3 to 30 % by weight (calculated as Co) based on the weight of the magnetic acicular metal particles; aluminum of usually 0.05 to 10 % by weight, preferably 0.1 to 7 % by weight (calculated as Al) based on the weight of the magnetic acicular metal particles; and at least one selected from the group consisting of Nd, La and Y of usually 0.05 to 10 % by weight, preferably 0.1 to 7 % by weight (calculated as the corresponding element) based on the weight of the magnetic acicular metal particles.

7) Magnetic acicular metal particles comprises iron; cobalt of usually 0.05 to 40 % by weight, preferably 1.0 to 35 % by weight, more preferably 3 to 30 % by weight (calculated as Co) based on the weight of the magnetic acicular metal particles; and at least one selected from the group consisting of Ni, P, Si, Zn, Ti, Cu and B of usually 0.05 to 10 % by weight, preferably 0.1 to 7 % by weight (calculated as the corresponding element) based on the weight of the magnetic acicular metal particles.

8) Magnetic acicular metal particles comprises iron; aluminum of usually 0.05 to 10 % by weight, preferably 0.1 to 7 % by weight (calculated as Al) based on the weight of the magnetic acicular metal particles; and at least one selected from the group consisting of Ni, P, Si, Zn, Ti, Cu and B of usually 0.05 to 10 % by weight, preferably 0.1 to 7 % by weight (calculated as the corresponding element) based on the weight of the magnetic acicular metal particles.

9) Magnetic acicular metal particles comprises iron; cobalt of usually 0.05 to 40 % by weight, preferably 1.0 to 35 % by weight, more preferably 3 to 30 % by weight (calculated as Co) based on the weight of the magnetic acicular

metal particles; aluminum of usually 0.05 to 10 % by weight, preferably 0.1 to 7 % by weight (calculated as Al) based on the weight of the magnetic acicular metal particles; and at least one selected from the group consisting of Ni, P, Si, Zn, Ti, Cu and B of usually 0.05 to 10 % by weight, preferably 0.1 to 7 % by weight (calculated as the corresponding element) based on the weight of the magnetic acicular metal particles.

10) Magnetic acicular metal particles comprises iron; cobalt of usually 0.05 to 40 % by weight, preferably 1.0 to 35 % by weight, more preferably 3 to 30 % by weight (calculated as Co) based on the weight of the magnetic acicular metal particles; at least one selected from the group consisting of Nd, La and Y of usually 0.05 to 10 % by weight, preferably 0.1 to 7 % by weight (calculated as the corresponding element) based on the weight of the magnetic acicular metal particles; and at least one selected from the group consisting of Ni, P, Si, Zn, Ti, Cu and B of usually 0.05 to 10 % by weight, preferably 0.1 to 7 % by weight (calculated as the corresponding element) based on the weight of the magnetic acicular metal particles.

11) Magnetic acicular metal particles comprises iron; aluminum of usually 0.05 to 10 % by weight, preferably 0.1 to 7 % by weight (calculated as Al) based on the weight of the magnetic acicular metal particles; at least one selected from the group consisting of Nd, La and Y of usually 0.05 to 10 % by weight, preferably 0.1 to 7 % by weight (calculated as the corresponding element) based on the weight of the magnetic acicular metal particles; and at least one selected from the group consisting of Ni, P, Si, Zn, Ti, Cu and B of usually 0.05 to 10 % by weight, preferably 0.1 to 7 % by weight (calculated as the corresponding element) based on the weight of the magnetic acicular metal particles.

12) Magnetic acicular metal particles comprises iron; cobalt of usually 0.05 to 40 % by weight, preferably 1.0 to 35 % by weight, more preferably 3 to 30 % by weight (calculated as Co) based on the weight of the magnetic acicular metal particles; aluminum of usually 0.05 to 10 % by weight, preferably 0.1 to 7 % by weight (calculated as Al) based on the weight of the magnetic acicular metal particles; at least one selected from the group consisting of Nd, La and Y of usually 0.05 to 10 % by weight, preferably 0.1 to 7 % by weight (calculated as the corresponding element) based on the weight of the magnetic acicular metal particles; and at least one selected from the group consisting of Ni, P, Si, Zn, Ti, Cu and B of usually 0.05 to 10 % by weight, preferably 0.1 to 7 % by weight (calculated as the corresponding element) based on the weight of the magnetic acicular metal particles.

[0037] The iron content in the magnetic acicular metal particles is the balance, and is preferably 50 to 99 % by weight; more preferably 60 to 95 % by weight (calculated as Fe) based on the weight of magnetic acicular metal particles.

[0038] The shape of the core particles used in the present invention have substantially acicular. The "acicular" shape may include not only a needle shape but also a spindle shape or a rice-ball shape.

[0039] The average major axis diameter of the magnetic acicular particles as core particles used in the present invention is usually 0.05 to 0.7 μm , preferably 0.05 to 0.5 μm , more preferably 0.05 to 0.3 μm .

[0040] When the average major axis diameter of the magnetic acicular particles is more than 0.7 μm , the obtained black magnetic acicular composite particles also may become large particles. In the case where such large particles are used for forming a magnetic recording layer, the surface smoothness of the magnetic recording layer tends to be deteriorated. On the other hand, when the average particle size is less than 0.05 μm , the intermolecular force between the particles may be increased due to the reduction in particle size, so that agglomeration of the particles tends to be caused. Therefore, it becomes difficult to uniformly coat the surfaces of the magnetic acicular particle with the organosilicon compound, and to uniformly adhere the carbon black fine particles on the surface of the coating comprising the organosilicon compounds.

[0041] The average minor axis diameter of the magnetic acicular particles as core particles used in the present invention is preferably 0.025 to 0.35 μm , more preferably 0.025 to 0.25 μm , still more preferably 0.025 to 0.15 μm .

[0042] The aspect ratio of the magnetic acicular particles as core particles used in the present invention (= average major axis diameter : average minor axis diameter, hereinafter referred to merely as "aspect ratio") is usually 2.0:1 to 20.0:1, preferably 2.5:1 to 18.0:1, more preferably 3.0:1 to 15.0:1. When the aspect ratio is more than 20.0:1, the magnetic acicular particles tend to be entangled with each other, and it also becomes difficult to uniformly coat the surfaces of the magnetic acicular particles with the organosilicon compounds and to uniformly adhere the carbon black fine particles on the surface of the coating comprising the organosilicon compounds. On the other hand, when the aspect ratio is less than 2.0:1, the strength of the coating film of the magnetic recording medium may be low.

[0043] The geometrical standard deviation value of the major axis diameter of the magnetic acicular particles as core particles used in the present invention is usually not more than 2.0, preferably not more than 1.8, more preferably not more than 1.6. When the geometrical standard deviation value thereof is more than 2.0, coarse particles may be contained therein, so that the magnetic acicular particles may be inhibited from being uniformly dispersed. Therefore, it also becomes difficult to uniformly coat the surfaces of the magnetic acicular particles with the organosilicon compounds and to uniformly adhere the carbon black fine particles on the surface of the coating comprising the organosilicon compounds. The lower limit of the geometrical standard deviation value is 1.01. It is industrially difficult to obtain particles having a geometrical standard deviation value of less than 1.01.

[0044] The BET specific surface area of the magnetic acicular particles as core particles used in the present invention is usually 15 to 150 m²/g, preferably 20 to 120 m²/g, more preferably 25 to 100 m²/g. When the BET specific surface area is less than 15 m²/g, the magnetic acicular particles may become coarse, or the sintering between the particles may be caused, so that the obtained black magnetic acicular composite particles also may become coarse particles and tend to be deteriorated in smooth surface of the magnetic recording layer. When the BET specific surface area value is more than 150 m²/g, the particles tend to be agglomerated together due to the increase in intermolecular force between the particles because of the fineness thereof, so that it becomes difficult to uniformly coat the surfaces of the magnetic acicular particles with the organosilane compounds and to uniformly adhere the carbon black fine particles on the surface of the coating comprising the organosilicon compounds.

[0045] The blackness of the magnetic acicular particles as core particles used in the present invention, is usually more than 18.0 when represented by L* value, and the upper limit thereof is usually 34.0, preferably 32.0 when represented by L* value. When the L* value exceeds 34.0, the lightness of the particles may be high, so that it is difficult to obtain black magnetic acicular composite particles having a sufficient blackness.

[0046] The volume resistivity of the magnetite acicular particles as core particles used in the present invention is usually not more than 5.0×10^{10} Ω·cm, preferably not more than 1.0×10^{10} Ω·cm. The lower limit thereof is preferably about 1.0×10^6 Ω·cm.

[0047] As to the magnetic properties of the magnetic acicular particles as core particles used in the present invention, the coercive force value thereof is usually 250 to 3500 Oe, the saturation magnetization value is usually 60 to 170 emu/g.

[0048] In case of magnetic acicular iron oxide particles, the coercive force value thereof is usually 250 to 500 Oe, preferably 300 to 500 Oe; the saturation magnetization value is usually 60 to 90 emu/g, preferably 65 to 90 emu/g. In case of magnetic acicular cobalt-coated iron oxide particles, the coercive force value thereof is usually 500 to 1700 Oe, preferably 550 to 1700 Oe; the saturation magnetization value is usually 60 to 90 emu/g, preferably 65 to 90 emu/g. In case of magnetic acicular metal particles containing iron as a main component, the coercive force value thereof is usually 800 to 3500 Oe, preferably 900 to 3500 Oe; the saturation magnetization value is usually 90 to 170 emu/g, preferably 100 to 170 emu/g.

[0049] The particle shape and particle size of the black magnetic acicular composite particles according to the present invention are considerably varied depending upon those of the magnetic acicular particles as core particles. The black magnetic acicular composite particles have a similar particle shape to that of the magnetic acicular particle as core particle, and a slightly larger particle size than that of the magnetic acicular particles as core particles.

[0050] More specifically, the black magnetic acicular composite particles according to the present invention, have an average major axis diameter of usually 0.051 to 0.72 μm, preferably 0.051 to 0.51 μm, more preferably 0.051 to 0.31 μm and an aspect ratio of usually 2.0:1 to 20.0:1, preferably 2.5:1 to 18.0:1, more preferably 3.0:1 to 15.0:1. The minor axis diameter thereof is preferably 0.0255 to 0.36 μm, more preferably 0.0255 to 0.255 μm, still more preferably 0.0255 to 0.155 μm.

[0051] When the average particle size of the black magnetic acicular composite particles is more than 0.72 μm, the black magnetic acicular composite particles may become coarse and to be deteriorated in surface smooth. On the other hand, when the average particle size thereof is less than 0.051 μm, the black magnetic acicular composite particles tends to be agglomerated by the increase of intermolecular force due to the reduction in particle size, thereby deteriorating the dispersibility in a vehicle upon production of the magnetic coating composition.

[0052] When the aspect ratio of the black magnetic acicular composite particles is more than 20.0:1, the particles tend to be frequently entangled or intertwined with each other. As a result, upon the production of a magnetic coating composition, there is a tendency that the dispersibility of the particles in vehicle is deteriorated and the viscosity of the obtained magnetic coating composition is increased. On the other hand, when the aspect ratio thereof is less than 2.0:1, the strength of the coating film of the obtained magnetic recording medium is low.

[0053] The geometrical standard deviation value of the black magnetic acicular composite particles according to the present invention is preferably not more than 2.0. When the geometrical standard deviation value thereof is more than 2.0, the surface smooth of the magnetic recording layer of the magnetic recording medium is likely to be deteriorated due to the existence of coarse particles therein. With the consideration of the surface smooth of the magnetic recording layer, the geometrical standard deviation value thereof is more preferably not more than 1.8, still more preferably not more than 1.6. In the consideration of the industrial productivity, the lower limit of the geometrical standard deviation value thereof is preferably 1.01. It is industrially difficult to obtain such particles having a geometrical standard deviation of less than 1.01.

[0054] The BET specific surface area of the black magnetic acicular composite particles according to the present invention, is usually 16 to 160 m²/g, preferably 22 to 130 m²/g, more preferably 27 to 110 m²/g. When the BET specific surface area thereof is less than 16 m²/g, the black magnetic acicular composite particles may become coarse, and the sintering between the black magnetic acicular composite particles is caused, thereby deteriorating the surface smooth of the magnetic recording layer. On the other hand, when the BET specific surface area is more than 160 m²/g, the black magnetic acicular composite particles tend to be agglomerated together by the increase in intermolecular

force due to the reduction in particle size, thereby deteriorating the dispersibility in the vehicle upon production of the magnetic coating composition.

[0055] As to the blackness of the black magnetic acicular composite particles according to the present invention, the upper limit of the blackness thereof is usually 23, preferably 22, more preferably 21 when represented by L* value. When the L* value thereof is more than 23, the lightness of the black magnetic acicular composite particles becomes high, so that the black magnetic acicular composite particles having a sufficient blackness may not be obtained. The lower limit of the blackness thereof is 15 when represented by L* value.

[0056] The volume resistivity of the black magnetic acicular composite particles is usually not more than 1.0×10^7 Ω -cm, preferably 1.0×10^4 to 5.0×10^6 Ω -cm, more preferably 1.0×10^4 to 1.0×10^6 Ω -cm. When the volume resistivity of the black magnetic acicular composite particles is more than 1.0×10^7 Ω -cm, it is difficult to sufficiently reduce the surface resistivity of the obtained magnetic recording medium.

[0057] The percentage of desorption of carbon black fine particles from the black magnetic acicular composite particles according to the present invention, is preferably not more than 20 %, more preferably not more than 10 %. When the desorption percentage of the carbon black fine particles is more than 20 %, the desorbed carbon black fine particles tend to hinder the black magnetic acicular composite particles from being uniformly dispersed in the vehicle upon production of the magnetic coating composition.

[0058] As the magnetic properties of the black magnetic acicular composite particles according to the present invention, the coercive force of the black magnetic acicular composite particles is usually 250 to 3500 Oe, the saturation magnetization thereof is 60 to 170 emu/g.

[0059] In case of using magnetic acicular iron oxide particle as the core particles, the coercive force thereof is usually 250 to 500 Oe, preferably 300 to 500 Oe; the saturation magnetization thereof is 60 to 90 emu/g, preferably 65 to 90 emu/g. In case of using magnetic acicular cobalt-coated iron oxide particle as the core particles, the coercive force of the black magnetic acicular composite particles is usually 500 to 1700 Oe, preferably 550 to 1700 Oe; the saturation magnetization thereof is 60 to 90 emu/g, preferably 65 to 90 emu/g. In case of magnetic acicular metal particles containing iron as a main component, the coercive force of the black magnetic acicular composite particles is usually 800 to 3500 Oe, preferably 900 to 3500 Oe; the saturation magnetization thereof is 90 to 170 emu/g, preferably 100 to 170 emu/g.

[0060] The coating formed on the surface of the core particle comprises at least one organosilicon compound selected from the group consisting of (1) organosilane compounds obtained by drying or heat-treating alkoxysilane compounds; (2) polysiloxanes, or modified polysiloxanes selected from the group consisting of (2-A) polysiloxanes modified with at least one compound selected from the group consisting of polyethers, polyesters and epoxy compounds (hereinafter referred to merely as "modified polysiloxanes"), and (2-B) polysiloxanes whose molecular terminal is modified with at least one group selected from the group consisting of carboxylic acid groups, alcohol groups and a hydroxyl group; and (3) fluoroalkyl organosilane compounds obtained by drying or heat-treating fluoroalkylsilane compounds.

[0061] The organosilane compounds (1) can be produced by drying or heat-treating alkoxysilane compounds represented by the formula (I):

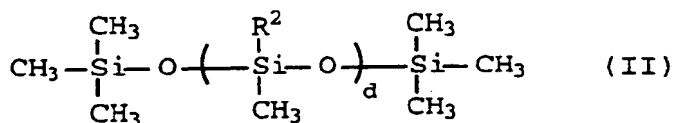


wherein R^1 is C_6H_5 -, $(CH_3)_2CHCH_2$ - or $n-C_bH_{2b+1}$ - (wherein b is an integer of 1 to 18); X is CH_3O - or C_2H_5O -; and a is an integer of 0 to 3.

[0062] The drying or heat-treatment of the alkoxysilane compounds is conducted, for example, at a temperature of usually 40 to 200°C, preferably 60 to 150°C for usually 10 minutes to 12 hours, preferably 30 minutes to 3 hours.

[0063] Specific examples of the alkoxysilane compounds may include methyl triethoxysilane, dimethyl diethoxysilane, tetraethoxysilane, phenyl triethoxysilane, diphenyl diethoxysilane, methyl trimethoxysilane, dimethyl dimethoxysilane, tetramethoxysilane, phenyl trimethoxysilane, diphenyl dimethoxysilane, isobutyl trimethoxysilane, decyl trimethoxysilane or the like. Among these alkoxysilane compounds, in view of the desorption percentage and the adhering effect of carbon black fine particles, methyl triethoxysilane, phenyl triethoxysilane, methyl trimethoxysilane, dimethyl dimethoxysilane and isobutyl trimethoxysilane are preferred, and methyl triethoxysilane and methyl trimethoxysilane are more preferred.

[0064] As the polysiloxanes (2), there may be used those compounds represented by the formula (II):

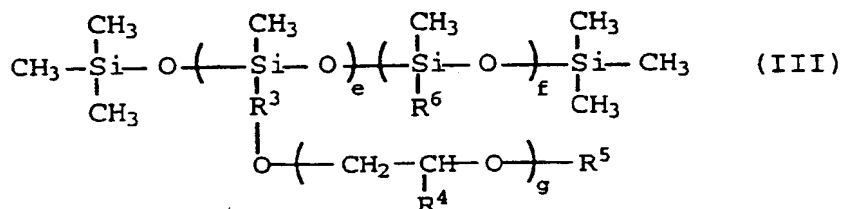


wherein R^2 is H - or CH_3 -, and d is an integer of 15 to 450.

[0065] Among these polysiloxanes, in view of the desorption percentage and the adhering effect of carbon black fine particles, polysiloxanes having methyl hydrogen siloxane units are preferred.

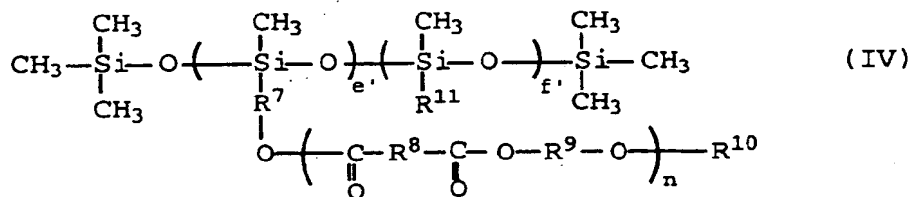
[0066] As the modified polysiloxanes (2-A), there may be used:

(a) polysiloxanes modified with polyethers represented by the formula (III):



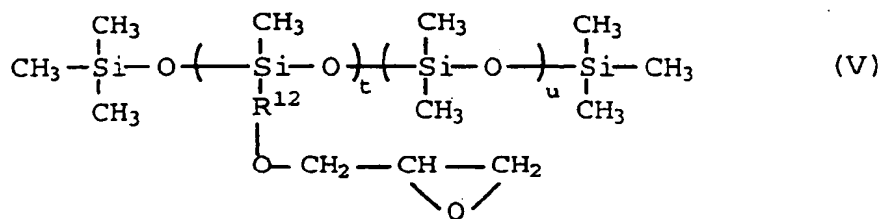
wherein R^3 is $-(\text{CH}_2)_h-$; R^4 is $-(\text{CH}_2)_i-\text{CH}_3$; R^5 is $-\text{OH}$, $-\text{COOH}$, $-\text{CH}=\text{CH}_2$, $-\text{C}(\text{CH}_3)=\text{CH}_2$ or $-(\text{CH}_2)_j-\text{CH}_3$; R^6 is $-(\text{CH}_2)_k-\text{CH}_3$; g and h are an integer of 1 to 15; i , j and k are an integer of 0 to 15; e is an integer of 1 to 50; and f is an integer of 1 to 300;

(b) polysiloxanes modified with polyesters represented by the formula (IV):



wherein R^7 , R^8 and R^9 are $-(\text{CH}_2)_q-$ and may be the same or different; R^{10} is $-\text{OH}$, $-\text{COOH}$, $-\text{CH}=\text{CH}_2$, $-\text{C}(\text{CH}_3)=\text{CH}_2$ or $-(\text{CH}_2)_r-\text{CH}_3$; R^{11} is $-(\text{CH}_2)_s-\text{CH}_3$; n and q are an integer of 1 to 15; r and s are an integer of 0 to 15; e' is an integer of 1 to 50; and f' is an integer of 1 to 300;

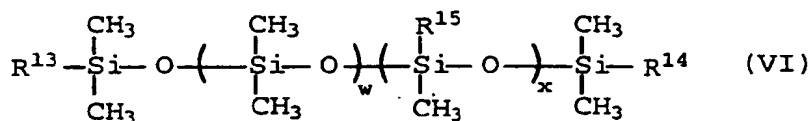
(c) polysiloxanes modified with epoxy compounds represented by the formula (V):



wherein R^{12} is $-(\text{CH}_2)_v-$; v is an integer of 1 to 15; t is an integer of 1 to 50; and u is an integer of 1 to 300; or a mixture thereof.

[0067] Among these modified polysiloxanes (2-A), in view of the desorption percentage and the adhering effect of carbon black fine particles, the polysiloxanes modified with the polyethers represented by the formula (III), are preferred.

[0068] As the terminal-modified polysiloxanes (2-B), there may be used those represented by the formula (VI):



wherein R^{13} and R^{14} are $-\text{OH}$, R^{16}OH or R^{17}COOH and may be the same or different; R^{15} is $-\text{CH}_3$ or $-\text{C}_6\text{H}_5$; R^{16} and R^{17} are $-(\text{CH}_2)_y-$; y is an integer of 1 to 15; w is an integer of 1 to 200; and x is an integer of 0 to 100.

[0069] Among these terminal-modified polysiloxanes, in view of the desorption percentage and the adhering effect of carbon black fine particles, the polysiloxanes whose terminals are modified with carboxylic acid groups are preferred.

[0070] The fluoroalkyl organosilane compounds (3) may be produced by drying or heat-treating fluoroalkylsilane compounds represented by the formula (VII):



wherein R^{18} is CH_3- , C_2H_5- , $\text{CH}_3\text{O}-$ or $\text{C}_2\text{H}_5\text{O}-$; X is $\text{CH}_3\text{O}-$ or $\text{C}_2\text{H}_5\text{O}-$; and z is an integer of 0 to 15; and a is an integer of 0 to 3.

[0071] The drying or the heat-treatment of the fluoroalkylsilane compounds may be conducted, for example, at a temperature of usually 40 to 200°C, preferably 60 to 150°C for usually 10 minutes to 12 hours, preferably 30 minutes to 3 hours.

[0072] Specific examples of the fluoroalkylsilane compounds may include trifluoropropyl trimethoxysilane, tridecafluorooctyl trimethoxysilane, heptadecafluorodecyl trimethoxysilane, heptadecafluorodecylmethyl dimethoxysilane, trifluoropropyl triethoxysilane, tridecafluorooctyl triethoxysilane, heptadecafluorodecyl triethoxysilane, heptadecafluorodecylmethyl diethoxysilane or the like. Among these fluoroalkylsilane compounds, in view of the desorption percentage and the adhering effect of carbon black fine particles, trifluoropropyl trimethoxysilane, tridecafluorooctyl trimethoxysilane and heptadecafluorodecyl trimethoxysilane are preferred, and trifluoropropyl trimethoxysilane and tridecafluorooctyl trimethoxysilane are more preferred.

[0073] The coating amount of the organosilicon compounds is usually 0.02 to 5.0 % by weight, preferably 0.03 to 4.0 % by weight, more preferably 0.05 to 3.0 % by weight (calculated as Si) based on the weight of the magnetic acicular particles coated with the organosilicon compounds.

[0074] When the coating amount of the organosilicon compounds is less than 0.02 % by weight, it becomes difficult to adhere the carbon black fine particles on the surfaces of the magnetic acicular particles in such an amount enough to improve the blackness of the obtained black magnetic acicular composite particles.

[0075] On the other hand, when the coating amount of the organosilicon compounds is more than 5.0 % by weight,

a sufficient amount of the carbon black fine particles can be adhered on the surfaces of the magnetic acicular particles. However, the use of such unnecessarily large amount of the organosilicon compounds is meaningless because the effect of enhancing the blackness of the obtained black magnetic acicular composite particles is already saturated.

[0076] As the carbon black fine particles used in the black magnetic acicular composite particles according to the present invention, there may be exemplified commercially available carbon black particles such as furnace black, channel black or the like. Specific examples of the commercially available carbon black particles usable in the present invention, may include MA100, MA7, #1000, #2400B, #30, MA8, MA11, #50, #52, #45, #2200B, #3150, #3250, MA600, etc. (tradenames; produced by Mitsubishi Chemical Corp.), Seast9H, Seast7H, Seast6, Seast3H, Seast300, SeastFM, etc. (tradenames; produced by Tokai Carbon Co., Ltd.) or the like. In the consideration of compatibility with the organosilicon compounds, MA100, MA7, #1000, #2400B and #30 are preferred. Further, in the consideration of the volume resistivity of the black magnetic acicular composite particles, #3150 and #3250 are more preferred.

[0077] The average particle size of the carbon black fine particles is usually about 0.002 to about 0.05 μm , preferably about 0.002 to about 0.035 μm .

[0078] When the average particle size of the carbon black fine particles is less than 0.002 μm , the carbon black fine particles are too fine to be well handled.

[0079] On the other hand, when the average particle size of the carbon black fine particles is more than 0.05 μm , the particle size of the carbon black fine particles becomes much larger than that of the magnetic acicular particles as core particles, thereby causing insufficient adhesion of the carbon black fine particles onto the coating composed of the organosilicon compounds, and increasing the desorption percentage of the carbon black fine particles. As a result, the obtained black magnetic acicular composite particles tend to be deteriorated in dispersibility in a vehicle upon the production of magnetic coating composition.

[0080] The ratio of the average particle size of the magnetic acicular particles to that of the carbon black fine particles is preferably not less than 2:1. When the ratio is less than 2:1, the particle size of the carbon black fine particles becomes considerably larger as compared to that of the magnetic acicular particles as core particles, thereby causing insufficient adhesion of the carbon black fine particles onto the coat composed of the organosilicon compounds, and increasing the desorption percentage of the carbon black fine particles. As a result, the obtained black magnetic acicular composite particles tend to be deteriorated in dispersibility in a vehicle upon the production of magnetic coating composition.

[0081] The amount of the carbon black fine particles adhered is 0.5 to 10 parts by weight based on 100 parts by weight of the magnetic acicular particles as core particles.

[0082] When the amount of the carbon black fine particles adhered is less than 0.5 part by weight, the amount of the carbon black fine particles adhered may be insufficient, so that it becomes difficult to obtain black magnetic acicular composite particles having a sufficient blackness.

[0083] On the other hand, when the amount of the carbon black fine particles adhered is more than 10 parts by weight, the obtained black magnetic acicular composite particles can show a sufficient blackness. However, since the amount of the carbon black fine particles adhered is considerably large, the carbon black fine particles tend to be desorbed from the coating composed of the organosilicon compound. As a result, the obtained black magnetic acicular composite particles tend to be deteriorated in dispersibility in a vehicle upon the production of magnetic coating composition.

[0084] At least a part of the surface of the magnetic acicular particle as a core particle used in the present invention may be coated with at least one selected from the group consisting of a hydroxide of aluminum, an oxide of aluminum, a hydroxide of silicon and an oxide of silicon. When the black magnetic acicular composite particles obtained by using as core particles the magnetic acicular particles which are coated with the above-described coating material, are dispersed in a vehicle, the treated particles have an affinity with the binder resin and it is more easy to obtain a desired dispersibility.

[0085] The amount of the hydroxide of aluminum, the oxide of aluminum, the hydroxide of silicon or the oxide of silicon used as the coating material is usually not more than 20 % by weight, preferably 0.01 to 20 % by weight (calculated as Al and/or SiO_2) based on the total weight of the magnetic acicular particles coated. If it is less than 0.01 % by weight (calculated as Al and/or SiO_2) based on the total weight of the magnetic acicular particles coated, the dispersibility-improving effect by coating therewith may be insufficient. If the amount exceeds 20 % by weight (calculated as Al and/or SiO_2) based on the total weight of the magnetic acicular particles coated, the dispersibility-improving effect by coating therewith becomes saturated, so that it is meaningless to add a coating material more than necessary. From the point of view of dispersibility in the vehicle and industrial productivity, the more preferable amount of coating material is 0.05 to 10 % by weight (calculated as Al and/or SiO_2) based on the total weight of the magnetic acicular particles coated.

[0086] The particle size, geometrical standard deviation value, BET specific surface area, blackness L^* value, volume resistivity, magnetic properties and desorption percentage of carbon black fine particles of the black magnetic acicular composite particles wherein the surface of the core particle is coated with the hydroxides and/or oxides of aluminum

and/or silicon according to the present invention, are substantially the same as those of the black magnetic acicular composite particles wherein the core particle is uncoated with the hydroxides and/or oxides of aluminum and/or silicon according to the present invention. In addition, the dispersibility in the vehicle of the of the black magnetic acicular composite particles wherein the surface of the core particle is coated with the hydroxides and/or oxides of aluminum and/or silicon is more improved as compared with that of the black magnetic acicular composite particles wherein the core particle is uncoated therewith.

[0087] Next, the magnetic recording medium according to the present invention is described.

[0088] The magnetic recording medium according to the present invention comprises:

- a non-magnetic base film; and
- a magnetic recording layer formed on the non-magnetic base film, comprising a binder resin and the black magnetic acicular composite particles.

[0089] As the non-magnetic base film, the following materials which are at present generally used for the production of a magnetic recording medium are usable as a raw material: a synthetic resin such as polyethylene terephthalate, polyethylene, polypropylene, polycarbonate, polyethylene naphthalate, polyamide, polyamideimide and polyimide; foil and plate of a metal such as aluminum and stainless steel; and various kinds of paper. The thickness of the non-magnetic base film varies depending upon the material, but it is usually about 1.0 to 300 μm , preferably 2.0 to 200 μm .

[0090] In the case of a magnetic disc, polyethylene terephthalate is usually used as the non-magnetic base film, and the thickness thereof is usually 50 to 300 μm , preferably 60 to 200 μm .

[0091] In a magnetic tape, when polyethylene terephthalate is used as the non-magnetic base film, the thickness thereof is usually 3 to 100 μm , preferably 4 to 20 μm ; when polyethylene naphthalate is used, the thickness thereof is usually 3 to 50 μm , preferably 4 to 20 μm ; and when polyamide is used, the thickness thereof is usually 2 to 10 μm , preferably 3 to 7 μm .

[0092] As the binder resin used in the present invention, the following resins which are at present generally used for the production of a magnetic recording medium are usable: vinyl chloride-vinyl acetate copolymer, urethane resin, vinyl chloride-vinyl acetate-maleic acid copolymer, urethane elastomer, butadiene-acrylonitrile copolymer, polyvinyl butyral, cellulose derivative such as nitrocellulose, polyester resin, synthetic rubber resin such as polybutadiene, epoxy resin, polyamide resin, polyisocyanate, electron radiation curing acryl urethane resin and mixtures thereof. Each of these resin binders may contain a functional group such as -OH, -COOH, -SO₃M, -OPO₂M₂ and -NH₂, wherein M represents H, Na or K. With the consideration of the dispersibility of the black magnetic acicular composite particles, a binder resin containing a functional group -COOH or -SO₃M is preferable.

[0093] The thickness of the magnetic recording layer obtained by applying the magnetic coating composition on the surface of the non-magnetic base film and dried, is usually in the range of 0.01 to 5.0 μm . If the thickness is less than 0.01 μm , uniform coating may be difficult, so that unfavorable phenomenon such as unevenness on the coating surface is observed. On the other hand, when the thickness exceeds 5.0 μm , it may be difficult to obtain desired signal recording property due to an influence of diamagnetism. The preferable thickness is in the range of 0.1 to 4.0 μm .

[0094] The mixing ratio of the black magnetic acicular composite particles with the binder resin is usually 5 to 2000 parts by weight, preferably 100 to 1000 parts by weight based on 100 parts by weight of the binder resin.

[0095] When the amount of the black magnetic acicular composite particles blended is less than 5 parts by weight, the obtained magnetic coating composition contains a too small amount of the black magnetic acicular composite particles. As a result, when a coating film is produced from such a magnetic coating composition, it is not possible to obtain a coating film in which the black magnetic acicular composite particles are continuously dispersed, so that the surface smoothness and the strength of the coating film become unsatisfactory. On the other hand, when the amount of the black magnetic acicular composite particles blended is more than 2,000 parts by weight, the amount of the black magnetic acicular composite particles becomes too large relative to that of the binder resin, so that it is not possible to sufficiently disperse the black magnetic acicular composite particles in the magnetic coating composition. As a result, when a coating film is produced from such a magnetic coating composition, it is difficult to obtain a coating film having a sufficiently smooth surface. Further, since the black magnetic acicular composite particles cannot be sufficiently bound with each other by the binder resin, the obtained coating film tends to become brittle.

[0096] In the magnetic recording medium according to the present invention, the amount of carbon black fine particles added to the magnetic recording layer thereof can be reduced to usually less than 6 parts by weight, preferably less than 5 parts by weight, more preferably less than 3 parts by weight based on 100 parts by weight of the black magnetic acicular composite particles.

[0097] Further, in the case where the black magnetic acicular composite particles wherein a large amount of the carbon black fine particles can be adhered onto the surface thereof, especially in an amount of 7 to 10 parts by weight based on 100 parts by weight of the magnetic acicular particles, are used as magnetic particles, it can be expected to omit the addition of the carbon black fine particles to the magnetic recording layer.

[0098] Incidentally, the magnetic recording layer may optionally contain a lubricant, an abrasive, an anti-static agent and other additives which are usually used for the production of magnetic recording media, in an amount of 0.1 to 50 parts by weight based on 100 parts of the binder resin.

[0099] The magnetic recording medium according to the present invention has a coercive force of usually 250 to 3500 Oe; a squareness (residual magnetic flux density Br/saturation magnetic flux density Bm) of usually 0.85 to 0.95; a gloss (of the coating film) of usually 150 to 300 %; a surface roughness Ra (of the coating film) of usually not more than 12.0 nm; a Young's modulus (relative value to a commercially available video tape: AV T-120 produced by Victor Company of Japan, Limited) of usually 124 to 160; a linear adsorption coefficient (of the coating film) of usually 1.30 to 10.0 μm^{-1} ; and a surface resistivity of not more than $1.0 \times 10^{10} \Omega/\text{sq}$.

[0100] In case of using the black magnetic acicular composite particles as magnetic particles, wherein the magnetic acicular iron oxide particles are used as core particles, the magnetic recording medium according to the present invention has a coercive force of usually 250 to 500 Oe, preferably 300 to 500 Oe; a squareness (residual magnetic flux density Br/saturation magnetic flux density Bm) of usually 0.85 to 0.95, preferably 0.86 to 0.95; a gloss (of the coating film) of usually 150 to 300 %, preferably 160 to 300 %; a surface roughness Ra (of the coating film) of usually not more than 12.0 nm, preferably 2.0 to 11.0 nm, more preferably 2.0 to 10.0 nm, a Young's modulus (relative value to a commercially available video tape: AV T-120 produced by Victor Company of Japan, Limited) of usually 124 to 160, preferably 125 to 160; a linear adsorption coefficient (of the coating film) of usually 1.30 to 10.0 μm^{-1} , preferably 1.35 to 10.0 μm^{-1} ; and a surface resistivity of usually not more than $1.0 \times 10^{10} \Omega/\text{sq}$, preferably not more than $7.5 \times 10^9 \Omega/\text{sq}$, more preferably not more than $5.0 \times 10^9 \Omega/\text{sq}$.

[0101] In case of using the black magnetic acicular composite particles as magnetic particles, wherein the magnetic acicular cobalt-coated iron oxide particles are used as core particles, the magnetic recording medium according to the present invention has a coercive force of usually 500 to 1700 Oe, preferably 550 to 1700 Oe; a squareness (residual magnetic flux density Br/saturation magnetic flux density Bm) of usually 0.85 to 0.95, preferably 0.86 to 0.95; a gloss (of the coating film) of usually 160 to 300 %, preferably 165 to 300 %; a surface roughness Ra (of the coating film) of usually not more than 12.0 nm, preferably 2.0 to 11.0 nm, more preferably 2.0 to 10.0 nm, a Young's modulus (relative value to a commercially available video tape: AV T-120 produced by Victor Company of Japan, Limited) of usually 124 to 160, preferably 125 to 160; a linear adsorption coefficient (of the coating film) of usually 1.30 to 10.0 μm^{-1} , preferably 1.35 to 10.0 μm^{-1} ; and a surface resistivity of usually not more than $1.0 \times 10^{10} \Omega/\text{sq}$, preferably not more than $7.5 \times 10^9 \Omega/\text{sq}$, more preferably not more than $5.0 \times 10^9 \Omega/\text{sq}$.

[0102] In case of using the black magnetic acicular composite particles as magnetic particles, wherein the magnetic acicular metal particles containing iron are used as a main component as core particles, the magnetic recording medium according to the present invention has a coercive force of usually 800 to 3500 Oe, preferably 900 to 3500 Oe; a squareness (residual magnetic flux density Br/saturation magnetic flux density Bm) of usually 0.85 to 0.95, preferably 0.86 to 0.95; a gloss (of the coating film) of usually 180 to 300 %, preferably 190 to 300 %; a surface roughness Ra (of the coating film) of usually not more than 12.0 nm, preferably 2.0 to 11.0 nm, more preferably 2.0 to 10.0 nm, a Young's modulus (relative value to a commercially available video tape: AV T-120 produced by Victor Company of Japan, Limited) of usually 124 to 160, preferably 125 to 160; a linear adsorption coefficient (of the coating film) of usually 1.40 to 10.0 μm^{-1} , preferably 1.45 to 10.0 μm^{-1} ; and a surface resistivity of usually not more than $1.0 \times 10^{10} \Omega/\text{sq}$, preferably not more than $7.5 \times 10^9 \Omega/\text{sq}$, more preferably not more than $5.0 \times 10^9 \Omega/\text{sq}$.

[0103] In case of using the black magnetic acicular composite particles as magnetic particles, wherein the magnetic acicular iron oxide particles coated with hydroxides and/or oxides of aluminum and/or silicon are used as core particles, the magnetic recording medium according to the present invention has a coercive force of usually 250 to 500 Oe, preferably 300 to 500 Oe; a squareness (residual magnetic flux density Br/saturation magnetic flux density Bm) of usually 0.85 to 0.95, preferably 0.86 to 0.95; a gloss (of the coating film) of usually 155 to 300 %, preferably 165 to 300 %; a surface roughness Ra (of the coating film) of usually not more than 11.0 nm, preferably 2.0 to 10.0 nm, more preferably 2.0 to 9.0 nm, a Young's modulus (relative value to a commercially available video tape: AV T-120 produced by Victor Company of Japan, Limited) of usually 126 to 160, preferably 127 to 160; a linear adsorption coefficient (of the coating film) of usually 1.30 to 10.0 μm^{-1} , preferably 1.35 to 10.0 μm^{-1} ; and a surface resistivity of usually not more than $1.0 \times 10^{10} \Omega/\text{sq}$, preferably not more than $7.5 \times 10^9 \Omega/\text{sq}$, more preferably not more than $5.0 \times 10^9 \Omega/\text{sq}$.

[0104] In case of using the black magnetic acicular composite particles as magnetic particles, wherein the magnetic acicular cobalt-coated iron oxide particles which are coated with hydroxides and/or oxides of aluminum and/or silicon, are used as core particles, the magnetic recording medium according to the present invention has a coercive force of usually 500 to 1700 Oe, preferably 550 to 1700 Oe; a squareness (residual magnetic flux density Br/saturation magnetic flux density Bm) of usually 0.85 to 0.95, preferably 0.86 to 0.95; a gloss (of the coating film) of usually 165 to 300 %, preferably 170 to 300 %; a surface roughness Ra (of the coating film) of usually not more than 11.0 nm, preferably 2.0 to 10.0 nm, more preferably 2.0 to 9.0 nm, a Young's modulus (relative value to a commercially available video tape: AV T-120 produced by Victor Company of Japan, Limited) of usually 126 to 160, preferably 127 to 160; a linear adsorption coefficient (of the coating film) of usually 1.30 to 10.0 μm^{-1} , preferably 1.35 to 10.0 μm^{-1} ; and a surface resistivity

of usually not more than $1.0 \times 10^{10} \Omega/\text{sq}$, preferably not more than $7.5 \times 10^9 \Omega/\text{sq}$, more preferably not more than $5.0 \times 10^9 \Omega/\text{sq}$.

[0105] In case of using the black magnetic acicular composite particles as magnetic particles, wherein the magnetic acicular metal particles containing iron as a main component which are coated with hydroxides and/or oxides of aluminum and/or silicon, which are coated with hydroxides and/or oxides of aluminum and/or silicon, are used as core particles, the magnetic recording medium according to the present invention has a coercive force of usually 800 to 3500 Oe, preferably 900 to 3500 Oe; a squareness (residual magnetic flux density B_r /saturation magnetic flux density B_m) of usually 0.85 to 0.95, preferably 0.86 to 0.95; a gloss (of the coating film) of usually 185 to 300 %, preferably 195 to 300 %; a surface roughness R_a (of the coating film) of usually not more than 11.0 nm, preferably 2.0 to 10.0 nm, more preferably 2.0 to 9.0 nm, a Young's modulus (relative value to a commercially available video tape: AV T-120 produced by Victor Company of Japan, Limited) of usually 126 to 160, preferably 127 to 160; a linear adsorption coefficient (of the coating film) of usually 1.40 to $10.0 \mu\text{m}^{-1}$, preferably 1.45 to $10.0 \mu\text{m}^{-1}$; and a surface resistivity of usually not more than $1.0 \times 10^{10} \Omega/\text{sq}$, preferably not more than $7.5 \times 10^9 \Omega/\text{sq}$, more preferably not more than $5.0 \times 10^9 \Omega/\text{sq}$.

[0106] The black magnetic acicular composite particles according to the present invention can be produced by the following method.

[0107] Among the magnetic acicular particles used in the present invention, the acicular magnetite particles may be produced by passing an oxygen-containing gas through a suspension containing either ferric hydroxide colloid, iron carbonate or iron-containing precipitate, which is obtained by reacting an aqueous ferric salt solution with alkali hydroxide, alkali carbonate or both alkali hydroxide and alkali carbonate, while controlling the pH value and temperature of the suspension to produce acicular, spindle-shaped or rice-ball goethite particles, subjecting the obtained goethite particles to filtration, washing with water and drying, and then heat-reducing the thus treated goethite particles at a temperature of 300 to 800°C in a reducing gas atmosphere.

[0108] The acicular maghemite particles can be obtained by heating the above-mentioned magnetite particles in oxygen-containing gas at 300 to 600°C.

[0109] The magnetic acicular metal particles containing iron as a main component, can be obtained by heat-treating the above-mentioned acicular goethite particles or hematite particles obtained by heat-dehydrating the above-mentioned acicular goethite particles in a reducing gas at 300 to 500°C.

[0110] The coating of the magnetic acicular particles with the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, the terminal-modified polysiloxanes or the fluoroalkylsilane compounds, may be conducted by mechanically mixing and stirring the magnetic acicular particles together with the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, the terminal-modified polysiloxanes or the fluoroalkylsilane compounds; or by mechanically mixing and stirring both the components together while spraying the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, the terminal-modified polysiloxanes or the fluoroalkylsilane compounds onto the magnetic acicular particles. In these cases, substantially whole amount of the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, the terminal-modified polysiloxanes or the fluoroalkylsilane compounds added can be applied onto the surfaces of the magnetic acicular particles.

[0111] In order to uniformly coat the surfaces of the magnetic acicular particles with the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, the terminal-modified polysiloxanes or the fluoroalkylsilane compounds, it is preferred that the magnetic acicular particles are preliminarily diaggregated by using a pulverizer. As the apparatuses for the mixing and stirring, there may be used an edge runner, a Henschel mixer or the like.

[0112] The conditions for the mixing and stirring such as mixing ratio, linear load, stirring speed or mixing and stirring time, may be appropriately adjusted so as to coat the surfaces of the magnetic acicular particles with the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, the terminal-modified polysiloxanes or the fluoroalkylsilane compounds as uniformly as possible. The mixing and stirring time for the coating treatment is, for example, preferably not less than 20 minutes.

[0113] It is preferred that the acicular magnetite particles, the magnetic acicular metal particles containing iron as a main component which are susceptible to oxidation, be placed within a mixing device and purged with an inert gas such as N_2 in order to prevent the deterioration in magnetic properties thereof by the oxidation.

[0114] The amount of the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, the terminal-modified polysiloxanes or the fluoroalkylsilane compounds added, is preferably 0.15 to 45 parts by weight based on 100 parts by weight of the magnetic acicular particles. When the amount of the organosilicon compounds added is less than 0.15 part by weight, it may become difficult to adhere the carbon black fine particles in such an amount enough to improve the blackness and volume resistivity of the obtained black magnetic acicular composite particles. On the other hand, when the amount of the organosilicon compounds added is more than 45 parts by weight, a sufficient amount of the carbon black fine particles can be adhered on the surface of the coating, but it is meaningless because the blackness and volume resistivity of the obtained black magnetic acicular composite particles cannot be further improved by using such an excess amount of the organosilicon compounds.

[0115] Next, the carbon black fine particles are added to the magnetic acicular particles coated with the organosilicon compounds, and the resultant mixture is mixed and stirred to adhere the carbon black fine particles on the surfaces of the coating composed of the organosilicon compounds, and then dried.

[0116] In the case where the alkoxysilane compounds (1) and the fluoroalkylsilane compounds (3) are used as the coating compound, after the carbon black fine particles are adhered on the surface of the coating, the resultant composite particles are dried or heat-treated, for example, at a temperature of usually 40 to 200°C, preferably 60 to 150°C for usually 10 minutes to 12 hours, preferably 30 minutes to 3 hours, thereby forming a coating composed of the organosilane compounds (1) and the fluoroalkyl organosilane compounds (3), respectively.

[0117] It is preferred that the carbon black fine particles are added little by little and slowly, especially about 5 to 60 minutes.

[0118] The conditions for mixing and stirring the magnetic acicular particles coated with the organosilicon compounds and the carbon black fine particles, such as mixing ratio, linear load stirring speed or mixing and stirring time, may be appropriately adjusted so as to uniformly adhere the carbon black fine particles on the surface of the coating. The mixing and stirring time for the adhesion treatment is, for example, preferably not less than 20 minutes.

[0119] The amount of the carbon black fine particles added, is preferably 0.5 to 10 parts by weight based on 100 parts by weight of the magnetic acicular particles. When the amount of the carbon black fine particles added is less than 0.5 part by weight, it may become difficult to adhere the carbon black fine particles in such an amount enough to improve the blackness and volume resistivity of the obtained composite particles. On the other hand, when the amount of the carbon black fine particles added is more than 10 parts by weight, a sufficient blackness and volume resistivity of the resultant composite particles can be obtained, but the carbon black fine particles tend to be desorbed from the surface of the coating because of too large amount of the carbon black fine particles adhered, resulting in deteriorated dispersibility in the vehicle upon the production of the magnetic coating composition.

[0120] The magnetic acicular particles may be coated with at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon, if required, prior to mixing and stirring with the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, the terminal-modified polysiloxanes or the fluoroalkylsilane compounds.

[0121] The coating of the hydroxides and/or oxides of aluminum and/or silicon may be conducted by adding an aluminum compound, a silicon compound or both the compounds to a water suspension in which the magnetic acicular particles are dispersed, followed by mixing and stirring, and further adjusting the pH value of the suspension, if required, thereby coating the surfaces of the magnetic acicular particles with at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon. The thus obtained magnetic acicular particles coated with the hydroxides and/or oxides of aluminum and/or silicon are then filtered out, washed with water, dried and pulverized. Further, the particles coated with the hydroxides and/or oxides of aluminum and/or silicon may be subjected to post-treatments such as deaeration treatment and compaction treatment, if required.

[0122] As the aluminum compounds, there may be exemplified aluminum salts such as aluminum acetate, aluminum sulfate, aluminum chloride or aluminum nitrate, alkali aluminates such as sodium aluminate, alumina sols or the like.

[0123] The amount of the aluminum compound added is 0.01 to 20 % by weight (calculated as Al) based on the weight of the magnetic acicular particles. When the amount of the aluminum compound added is less than 0.01 % by weight, it may be difficult to sufficiently coat the surfaces of the magnetic acicular particles with hydroxides and/or oxides of aluminum, thereby failing to achieve the improvement of the dispersibility in the vehicle upon the production of the magnetic coating composition. On the other hand, when the amount of the aluminum compound added is more than 20 % by weight, the coating effect is saturated and, therefore, it is meaningless to add such an excess amount of the aluminum compound.

[0124] As the silicon compounds, there may be exemplified #3 water glass, sodium orthosilicate, sodium metasilicate, colloidal silica or the like.

[0125] The amount of the silicon compound added is 0.01 to 20 % by weight (calculated as SiO_2) based on the weight of the magnetic acicular particles. When the amount of the silicon compound added is less than 0.01 % by weight, it may be difficult to sufficiently coat the surfaces of the magnetic acicular particles with hydroxides and/or oxides of silicon, thereby failing to achieve the improvement of the dispersibility in the vehicle upon the production of the magnetic coating composition. On the other hand, when the amount of the silicon compound added is more than 20 % by weight, the coating effect is saturated and, therefore, it is meaningless to add such an excess amount of the silicon compound.

[0126] In the case where both the aluminum and silicon compounds are used in combination for the coating, the total amount of the aluminum and silicon compounds added is preferably 0.01 to 20 % by weight (calculated as a sum of Al and SiO_2) based on the weight of the magnetic acicular particles.

[0127] The process of the magnetic recording medium according to the present invention is described as follows.

[0128] The magnetic recording medium according to the present invention can be produced by applying a magnetic coating composition containing the black magnetic acicular composite particles, a binder resin and a solvent, on the non-magnetic base film, followed by drying, to form a magnetic recording layer thereon.

[0129] As the solvents, there may be used methyl ethyl ketone, toluene, cyclohexanone, methyl isobutyl ketone, tetrahydrofuran, a mixture of these solvents or the like.

[0130] The total amount of the solvent used is 65 to 1,000 parts by weight based on 100 parts by weight of the black magnetic acicular composite particles. When the amount of the solvent used is less than 65 parts by weight, the viscosity of the magnetic coating composition prepared therefrom becomes too high, thereby making it difficult to apply the magnetic coating composition. On the other hand, when the amount of the solvent used is more than 1,000 parts by weight, the amount of the solvent volatilized during the formation of the coating film becomes too large, thereby rendering the coating process industrially disadvantageous.

[0131] An important point of the present invention exists in that the black magnetic acicular composite particles comprising the magnetic acicular particles which may be coated with at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon; the organosilicon compounds coated on at least a part of the surface of the magnetic acicular particle; the carbon black fine particles having an average particle size of 0.002 to 0.05 μm , which are adhered on the surface of the coating comprising the organosilicon compounds, in which the total amount of the carbon black fine particles adhered to the coating comprising the organosilicon compounds is 0.5 to 10 parts by weight based on 100 parts by weight of the magnetic acicular particles, can show excellent dispersibility in vehicle due to less amount of carbon black fine particles fallen-off from the surface of each black magnetic acicular composite particle, and have a high blackness and a low volume resistivity.

[0132] The reason why the black magnetic acicular composite particles according to the present invention can show an excellent blackness, is considered such that since the carbon black fine particles are uniformly and densely adhered on the surfaces of the magnetic acicular particles, the color tone of the core particles is hidden behind the carbon black fine particles, so that an inherent color tone of carbon black can be exhibited.

[0133] The reason why the black magnetic acicular composite particles according to the present invention can show a low volume resistivity is considered as follows. That is, the carbon black fine particles having an excellent conductivity can be uniformly and densely adhered onto the surface of each black magnetic acicular composite particle.

[0134] The reason why the amount of the carbon black fine particles desorbed or fallen-off from the surfaces of the black magnetic acicular composite particles according to the present invention, is small, is considered as follows. That is, the surfaces of the magnetic acicular particles and the organosilicon compounds are strongly bonded to each other, so that the carbon black fine particles bonded to the surfaces of the magnetic acicular particles through the organosilicon compounds can be prevented from being desorbed from the magnetic particles.

[0135] In particular, in the case of the alkoxysilane compounds (1) and the fluoroalkylsilane compounds (3), metallosiloxane bonds (Si-O-M wherein M represents a metal atom contained in the magnetic acicular particles, such as Si, Al, Fe or the like) are formed between the surfaces of the magnetic acicular particles and alkoxy groups contained in the organosilicon compounds onto which the carbon black fine particles are adhered, thereby forming a stronger bond between the organosilicon compounds on which the carbon black fine particles are adhered, and the surfaces of the magnetic acicular particles.

[0136] The reason why the black magnetic acicular composite particles according to the present invention can show an excellent dispersibility in a vehicle upon the production of magnetic coating composition, is considered such that since only a small amount of the carbon black fine particles are desorbed or fallen-off from the surfaces of the black magnetic acicular composite particles, the black magnetic acicular composite particles is free from deterioration in dispersibility due to the desorbed or fallen-off carbon black fine particles, and further since the carbon black fine particles are adhered onto the surfaces of the black magnetic acicular composite particles and, therefore, irregularities are formed on the surfaces of the black magnetic acicular composite particles, the contact between the particles can be suppressed.

[0137] The magnetic recording medium according to the present invention which is obtained by using the above-mentioned black magnetic acicular composite particles as magnetic particles, can show a low light transmittance and a low surface resistivity even when the amount of carbon black fine particles in the magnetic recording layer is as small as possible, and the magnetic recording layer thereof can exhibit an improved surface smoothness.

[0138] The reason why the magnetic recording medium can show a low light transmittance even when the amount of carbon black fine particles is small, is considered as follows. That is, in the case of the black magnetic acicular composite particles according to the present invention, the carbon black fine particles which usually tend to be agglomerated together because of the fineness thereof, can be uniformly and densely adhered onto the surface of each magnetic acicular particle and, therefore, can be dispersed in the coating film in such a condition close to primary particles, whereby the individual carbon black fine particles can effectively exhibit their own functions.

[0139] The reason why the surface resistivity of the magnetic recording medium can be kept low even when the amount of carbon black fine particles is small, is considered as follows. That is, due to the fact that the black magnetic acicular composite particles are uniformly dispersed in the coating film, the carbon black fine particles uniformly and densely adhered onto the surfaces thereof are continuously contacted with each other.

[0140] The reason why the magnetic recording medium according to the present invention can show an excellent

surface smoothness, is considered as follows. That is, in the present invention, since the amount of the carbon black fine particles fallen-off from the surfaces of the black magnetic acicular composite particles is lessened and the amount of the carbon black fine particles added to the magnetic recording layer is reduced to as small a level as possible, the black magnetic acicular composite particles can maintain a good dispersibility in vehicle upon production of the magnetic coating composition without being adversely affected by the carbon black fine particles. Further, the black magnetic acicular composite particles themselves can exhibit an excellent dispersibility.

[0141] The black magnetic acicular composite particles according to the present invention, can show a high blackness, a low volume resistivity and an excellent dispersibility. Therefore, even though the amount of the carbon black fine particles added to the magnetic recording layer is reduced to as small a level as possible, it is possible to obtain a magnetic recording medium showing a low light transmittance, a low surface resistivity and a smooth surface. Accordingly, the black magnetic acicular composite particles can be suitably used as magnetic particles for high-density magnetic recording media.

[0142] As described above, due to the fact that the black magnetic acicular composite particles show an excellent blackness and a low volume resistivity, the magnetic recording medium according to the present invention can exhibit a low light transmittance and a low surface resistivity. Further, since the amount of carbon black fine particles added to the magnetic recording layer is reduced to as small a level as possible and the dispersibility of the black magnetic acicular composite particles themselves is enhanced, the magnetic recording medium can have a smooth surface. Therefore, the magnetic recording medium according to the present invention can be suitably used as those for high-density recording.

[0143] Furthermore, the magnetic recording medium according to the present invention is also preferred from the standpoints of safety and hygiene since the amount of the carbon black fine particles used therein can be reduced.

EXAMPLES

[0144] The present invention is described in more detail by Examples and Comparative Examples, but the Examples are only illustrative and, therefore, not intended to limit the scope of the present invention.

[0145] Various properties were evaluated by the following methods.

[0146] (1) The average major axis diameter and average minor axis diameter of magnetic acicular particles and black magnetic acicular composite particles, and average particle diameter of carbon black fine particles were respectively expressed by the average of values (measured in a predetermined direction) of about 350 particles which were sampled from a micrograph obtained by magnifying an original electron micrograph ($\times 20,000$) by four times in each of the longitudinal and transverse directions.

[0147] (2) The aspect ratio of the particles was expressed by the ratio of average major axis diameter to average minor axis diameter thereof.

[0148] (3) The geometrical standard deviation of major axis diameter was expressed by values obtained by the following method. That is, the major axis diameters were measured from the above-magnified electron micrograph. The actual major axis diameters and the number of the particles were calculated from the measured values. On a logarithmic normal probability paper, the major axis diameters were plotted at regular intervals on the abscissa-axis and the accumulative number (under integration sieve) of particles belonging to each interval of the major axis diameters were plotted by percentage on the ordinate-axis by a statistical technique.

[0149] The major axis diameters corresponding to the number of particles of 50 % and 84.13 %, respectively, were read from the graph, and the geometrical standard deviation was calculated from the following formula:

Geometrical standard deviation =

{major axis diameters corresponding to 84.13 % under integration sieve}/{major axis diameters

(geometrical average diameter) corresponding

to 50 % under integration sieve}

[0150] The closer to 1 the geometrical standard deviation value, the more excellent the particle size distribution.

[0151] (4) The specific surface area was expressed by the value measured by a BET method.

[0152] (5) The amounts of Al, Si and Co which were present within magnetic acicular particles or black magnetic acicular composite particles or on surfaces thereof, and the amount of Si contained in the organosilicon compounds, were measured by a fluorescent X-ray spectroscopy device 3063 (manufactured by Rigaku Denki Kogyo Co., Ltd.)

according to JIS K0119 "General rule of fluorescent X-ray analysis".

[0153] (6) The content of Fe²⁺ in the magnetic acicular particles is expressed by the value measured by the following chemical analysis method.

[0154] That is, 25 cc of a mixed solution composed of phosphoric acid and sulfuric acid at a mixing ratio of 2:1, was added to 0.5 g of magnetic acicular particles, thereby dissolving the magnetic acicular particles in the mixed solution. After several droplets of diphenylamine sulfonic acid as an indicator was added to the diluted solution, the solution was subjected to oxidation-reduction titration using an aqueous potassium bichromate solution. The titration was terminated when the diluted solution exhibited a violet color. The amount of Fe²⁺ was measured from the amount of the aqueous potassium bichromate solution used up to the termination of the titration.

[0155] (7) The amount of carbon adhered on the black magnetic acicular composite particles was measured by "Horiba Metal, Carbon and Sulfur Analyzer EMIA-2200 Model" (manufactured by Horiba Seisakusho Co., Ltd.).

[0156] (8) The blackness of magnetic acicular particles and black magnetic acicular composite particles was measured by the following method. That is, 0.5 g of sample particles and 1.5 cc of castor oil were intimately kneaded together by a Hoover's muller to form a paste. 4.5 g of clear lacquer was added to the obtained paste and was intimately kneaded to form a paint. The obtained paint was applied on a cast-coated paper by using a 6-mil applicator to produce a coating film piece (having a film thickness of about 30 μm). The thus obtained coating film piece was measured according to JIS Z 8729 by a multi-light source spectrographic colorimeter MSC-IS-2D (manufactured by Suga Testing Machines Manufacturing Co., Ltd.) to determine an L* value of colorimetric indices thereof. The blackness was expressed by the L* value measured.

[0157] Here, the L* value represents a lightness, and the smaller the L* value, the more excellent the blackness.

[0158] (9) The volume resistivity of the magnetic acicular particles and the black magnetic acicular composite particles was measured by the following method.

[0159] That is, first, 0.5 g of a sample particles to be measured was weighted, and press-molded at 140 Kg/cm² using a KBr tablet machine (manufactured by Simazu Seisakusho Co., Ltd.), thereby forming a cylindrical test piece.

[0160] Next, the thus obtained cylindrical test piece was exposed to an atmosphere maintained at a temperature of 25°C and a relative humidity of 60 % for 12 hours. Thereafter, the cylindrical test piece was set between stainless steel electrodes, and a voltage of 15V was applied between the electrodes using a Wheatstone bridge (model 4329A, manufactured by Yokogawa-Hokushin Denki Co., Ltd.) to measure a resistance value R (Ω).

[0161] The cylindrical test piece was measured with respect to an upper surface area A (cm²) and a thickness t₀ (cm) thereof. The measured values were inserted into the following formula, thereby obtaining a volume resistivity X (Ω·cm).

$$X (\Omega \cdot \text{cm}) = R \times (A/t_0)$$

[0162] (10) The desorption percentage of carbon black fine particles adhered on the black magnetic acicular composite particles was measured by the following method. The closer to zero the desorption percentage, the smaller the amount of carbon black fine particles desorbed from the surfaces of black magnetic acicular composite particles.

[0163] That is, 3 g of the black magnetic acicular composite particles and 40 ml of ethanol were placed in a 50-ml precipitation pipe and then was subjected to ultrasonic dispersion for 20 minutes. Thereafter, the obtained dispersion was allowed to stand for 120 minutes, and the carbon black fine particles desorbed were separated from the black magnetic acicular composite particles on the basis of the difference in specific gravity between both the particles. Next, the black magnetic acicular composite particles from which the desorbed carbon black fine particles were separated, were mixed again with 40 ml of ethanol, and the obtained mixture was further subjected to ultrasonic dispersion for 20 minutes. Thereafter, the obtained dispersion was allowed to stand for 120 minutes, thereby separating the black magnetic acicular composite particles and the desorbed carbon black desorbed from each other. The thus obtained black magnetic acicular composite particles were dried at 100°C for one hour, and then the carbon content thereof was measured by the "Horiba Metal, Carbon and Sulfur Analyzer EMIA-2200 Model" (manufactured by Horiba Seisakusho Co., Ltd.). The desorption percentage of the carbon black fine particles was calculated according to the following formula:

Desorption percentage of carbon black fine particles

$$= \{(W_a - W_e)/W_a\} \times 100$$

wherein W_a represents an amount of carbon black fine particles initially adhered on the black magnetic acicular composite particles; and W_e represents an amount of carbon black fine particles still adhered on the black magnetic acicular

composite particles after desorption test.

[0164] (11) The viscosity of the coating composition was obtained by measuring the viscosity of the coating composition at 25°C at a shear rate D of 1.92 sec^{-1} by using "E type viscometer EMD-R" (manufactured by Tokyo Keiki, Co., Ltd.).

[0165] (12) The gloss of the surface of the coating film of the magnetic recording layer was measured at an angle of incidence of 45° by "glossmeter UGV-5D" (manufactured by Suga Shikenki, Co., Ltd.).

[0166] (13) The surface roughness R_a is expressed by the average value of the center-line average roughness of the profile curve of the surface of the coating film of the magnetic recording layer by using "Surfcom-575A" (manufactured by Tokyo Seimitsu Co., Ltd.).

[0167] (14) The strength of the coating film of the magnetic recording layer was expressed the Young's modulus obtained by "Autograph" (produced by Shimazu Seisakusho Co., Ltd.). The Young's modulus was expressed by the ratio of the Young's modulus of the coating film to that of a commercially available video tape "AV T-120" (produce by Victor Company of Japan, Limited). The higher the relative value, the more favorable.

[0168] (15) The magnetic properties of the magnetic acicular particles, black magnetic acicular composite particles and magnetic recording medium were measured under an external magnetic field of 10 kOe by "Vibration Sample Magnetometer VSM-3S-15 (manufactured by Toei Kogyo, Co., Ltd.)."

[0169] (16) The light transmittance is expressed by the linear adsorption coefficient calculated by substituting the light transmittance measured by using "UV-Vis Recording Spectrophotometer UV-2100" (manufactured by Shimazu Seisakusho, Ltd.) for the following formula. The larger the value, the more difficult it is for the magnetic recording medium to transmit light:

[0170] Linear adsorption coefficient (μm^{-1}) = $\{1 - (1/t)\}/FT$ wherein t represents a light transmittance (-) at $\lambda = 900 \text{ nm}$, and FT represents thickness (pm) of the coating film used for the measurement.

[0171] (17) The surface resistivity of the coating film of the magnetic recording layer was measured by the following method. That is, the coating film to be measured was exposed to the environment maintained at a temperature of 25°C and a relative humidity of 60 %, for not less than 12 hours. Thereafter, the coating film was slit into 6 mm width, and the slit coating film was placed on two metal electrodes having a width of 6.5 mm such that a coating surface thereof was contacted with the electrodes. 170-gram weights were respectively suspended at opposite ends of the coating film so as to bring the coating film into close contact with the electrodes. D.C. 500 V was applied between the electrodes, thereby measuring the surface resistivity of the coating film.

[0172] (18) The thickness of each of the non-magnetic base film and the magnetic recording layer constituting the magnetic recording medium was measured in the following manner by using "Digital Electronic Micrometer R351C" (manufactured by Anritsu Corp.)

[0173] The thickness (A) of a non-magnetic base film was first measured. Similarly, the thickness (B) (B = the sum of the thicknesses of the non-magnetic base film and the magnetic recording layer) of a magnetic recording medium obtained by forming a magnetic recording layer on the non-magnetic base film was measured. The thickness of the magnetic recording layer is expressed by (B) - (A).

Example 1:

<Production of black magnetic acicular composite particles>

[0174] 20 kg of acicular cobalt-coated magnetite particles shown in the electron micrograph ($\times 30,000$) of Fig. 1 (cobalt content: 2.21 % by weight based on the weight of the acicular cobalt-coated magnetite particles; Fe^{2+} content: 15.8 % by weight based on the weight of the acicular cobalt-coated magnetite particles; average major axis diameter: 0.278 μm ; average minor axis diameter: 0.0330 μm ; aspect ratio: 8.4:1; geometrical standard deviation value: 1.38; BET specific surface area value: 38.7 m^2/g ; blackness (L^* value): 22.6; volume resistivity: $7.3 \times 10^7 \Omega\text{-cm}$; coercive force value: 686 Oe; saturation magnetization value: 79.1 emu/g), were deagglomerated in 150 liters of pure water using a stirrer, and further passed through a "TK pipeline homomixer" (tradename, manufactured by Tokushu Kika Kogyo Co., Ltd.) three times, thereby obtaining a slurry containing the acicular cobalt-coated magnetite particles.

[0175] Successively, the obtained slurry containing the acicular cobalt-coated magnetite particles was passed through a transverse-type sand grinder (tradename "MIGHTY MILL MHG-1.5L", manufactured by Inoue Seisakusho Co., Ltd.) five times at an axis-rotating speed of 2,000 rpm, thereby obtaining a slurry in which the acicular cobalt-coated magnetite particles were dispersed.

[0176] The particles in the obtained slurry which remained on a sieve of 325 meshes (mesh size: 44 μm) was 0 %. The slurry was filtered and washed with water, thereby obtaining a filter cake containing the acicular cobalt-coated magnetite particles. After the obtained filter cake containing the acicular cobalt-coated magnetite particles was dried at 120°C, 11.0 kg of the dried particles were then charged into an edge runner "MPUV-2 Model" (tradename, manufactured by Matsumoto Chuzo Tekkosho Co., Ltd.), and mixed and stirred at 30 Kg/cm for 15 minutes, while introducing

nitrogen gas thereinto at a rate of 2 liter/minute, thereby lightly deagglomerating the particles.

[0177] 220 g of methyl triethoxysilane was mixed and diluted with 200 ml of ethanol to obtain a methyl triethoxysilane solution. The methyl triethoxysilane solution was added to the deagglomerated acicular cobalt-coated magnetite particles under the operation of the edge runner. The acicular cobalt-coated magnetite particles were continuously mixed and stirred at a linear load of 30 Kg/cm for 20 minutes.

[0178] Next, 550 g of carbon black fine particles shown in the electron micrograph ($\times 30,000$) of Fig. 2 (particle shape: granular shape; average particle size: 0.022 μm ; geometrical standard deviation value: 1.68; BET specific surface area value: 134 m^2/g ; and blackness (L^* value): 16.6) were added to the acicular cobalt-coated magnetite particles coated with methyl triethoxysilane for 10 minutes while operating the edge runner. Further, the mixed particles were continuously stirred at a linear load of 30 Kg/cm for 30 minutes to adhere the carbon black fine particles on the coating composed of methyl triethoxysilane, thereby obtaining black magnetic acicular composite particles.

[0179] The obtained black magnetic acicular composite particles were aged at 80°C for 120 minutes by using a drier to evaporate water, ethanol or the like which were remained on surfaces of the black magnetic acicular composite particles. As shown in the electron micrograph ($\times 30,000$) of Fig. 3, the resultant black magnetic acicular composite particles had an average major axis diameter of 0.279 μm , an average minor axis diameter of 0.0335 μm , an aspect ratio of 8.3:1. In addition, the black magnetic acicular composite particles showed a geometrical standard deviation value of 1.38, a BET specific surface area value of 33.2 m^2/g , a blackness (L^* value) of 19.5 and a volume resistivity of $5.2 \times 10^4 \Omega\text{-cm}$. The desorption percentage of the carbon black fine particles from the black magnetic acicular composite particles was 6.8 %. As to the magnetic properties, the coercive force value of the black magnetic acicular composite particles was 672 Oe and the saturation magnetization value was 77.3 emu/g. The coating amount of an organosilane compound produced from methyl triethoxysilane was 0.31 % by weight calculated as Si. Since no independent carbon black fine particles were observed on the electron micrograph of Fig. 3, it was determined that a whole amount of the carbon black fine particles were adhered on the coating composed of the organosilane compound produced from methyl triethoxysilane.

[0180] Meanwhile, for comparison, the acicular cobalt-coated magnetite particles uncoated with the organosilicon compound and the carbon black fine particles were mixed and stirred together by an edge runner in the same manner as described above, thereby obtaining mixed particles. An electron micrograph ($\times 30,000$) of the thus treated particles is shown in Fig. 4. As shown in Fig. 4, it was confirmed that the carbon black fine particles were not adhered on the surfaces of the acicular cobalt-coated magnetite particles, and both the particles were present independently.

<Production of magnetic recording medium: Formation of magnetic recording layer>

[0181] 12 g of the thus obtained black magnetic acicular composite particles, 1.2 g of a polishing agent (AKP-30: trade name, produced by Sumitomo Chemical Co., Ltd.), 0.06 g of carbon black (#3250B, trade name, produced by Mitsubishi Chemical Corp.), a binder resin solution (30 % by weight of vinyl chloride-vinyl acetate copolymer resin having a sodium sulfonate group and 70 % by weight of cyclohexanone) and cyclohexanone were mixed to obtain a mixture (solid content: 78 % by weight). The mixture was further kneaded by a plast-mill for 30 minutes to obtain a kneaded material.

[0182] The thus-obtained kneaded material was charged into a 140 ml-glass bottle together with 95 g of 1.5 mm ϕ glass beads, a binder resin solution (30 % by weight of polyurethane resin having a sodium sulfonate group and 70 % by weight of a solvent (methyl ethyl ketone : toluene = 1 : 1)), cyclohexanone, methyl ethyl ketone and toluene, and the mixture was mixed and dispersed by a paint shaker for 6 hours. Then, the lubricant and hardening agent were added to the mixture, and the resultant mixture was mixed and dispersed by a paint shaker for 15 minutes.

[0183] The thus-obtained magnetic coating composition was as follows:

Black magnetic acicular composite particles	100 parts by weight
Vinyl chloride-vinyl acetate copolymer resin having a sodium sulfonate group	10 parts by weight
Polyurethane resin having a sodium sulfonate group	10 parts by weight
Polishing agent (AKP-30)	10 parts by weight
Carbon black (#3250B)	3.0 parts by weight
Lubricant (myristic acid: butyl stearate = 1 : 2)	3.0 parts by weight
Hardening agent (polyisocyanate)	5.0 parts by weight
Cyclohexanone	65.8 parts by weight
Methyl ethyl ketone	164.5 parts by weight
Toluene	98.7 parts by weight

[0184] The viscosity of the obtained magnetic coating composition was 2,304 cP.

[0185] The magnetic coating composition obtained was applied to a polyethylene terephthalate film (thickness: 12 μm) as a non-magnetic base film to a thickness of 45 μm by an applicator, and the magnetic recording medium obtained was oriented and dried in a magnetic field, and then calendered. The magnetic recording medium was then subjected to a curing reaction at 60°C for 24 hours, and thereafter slit into a width of 0.5 inch, thereby obtaining a magnetic tape. The thickness of the respective magnetic recording layer was 3.5 μm .

[0186] The coercive force value of the magnetic tape produced by forming a magnetic recording layer on the non-magnetic base film was 733 Oe, the squareness (Br/Bm) thereof was 0.89, the gloss thereof was 172 %, the surface roughness Ra thereof was 7.8 nm, the Young's modulus (relative value) thereof was 138, the linear absorption coefficient thereof was 1.48 μm^{-1} , and the surface resistivity was $1.3 \times 10^8 \Omega/\text{sq}$.

Example 2:

<Production of black magnetic acicular composite particles>

[0187] 20 kg of acicular cobalt-coated magnetite particles shown in the electron micrograph ($\times 30,000$) of Fig. 1 (cobalt content: 2.21 % by weight based on the weight of the acicular cobalt-coated magnetite particles; Fe^{2+} content: 15.8 % by weight based on the weight of the acicular cobalt-coated magnetite particles; average major axis diameter: 0.278 μm ; average minor axis diameter: 0.0330 μm ; aspect ratio: 8.4:1; geometrical standard deviation value: 1.38; BET specific surface area value: 38.7 m^2/g ; blackness (L^* value): 22.6; volume resistivity: $7.3 \times 10^7 \Omega\text{-cm}$; coercive force value: 686 Oe; saturation magnetization value: 79.1 emu/g), were deagglomerated in 150 liters of pure water using a stirrer, and further passed through a "TK pipeline homomixer" (tradename, manufactured by Tokushu Kika Kogyo Co., Ltd.) three times, thereby obtaining a slurry containing the acicular cobalt-coated magnetite particles.

[0188] Successively, the obtained slurry containing the acicular cobalt-coated magnetite particles was passed through a transverse-type sand grinder (tradename "MIGHTY MILL MHG-1.5L", manufactured by Inoue Seisakusho Co., Ltd.) five times at an axis-rotating speed of 2,000 rpm, thereby obtaining a slurry in which the acicular cobalt-coated magnetite particles were dispersed.

[0189] The particles in the obtained slurry which remained on a sieve of 325 meshes (mesh size: 44 μm) was 0 %. The slurry was filtered and washed with water, thereby obtaining a filter cake containing the acicular cobalt-coated magnetite particles. After the obtained filter cake containing the acicular cobalt-coated magnetite particles was dried at 120°C, 11.0 kg of the dried particles were then charged into an edge runner "MPUV-2 Model" (tradename, manufactured by Matsumoto Chuzo Tekkosho Co., Ltd.), and mixed and stirred at 30 Kg/cm for 15 minutes, while introducing nitrogen gas thereinto at a rate of 2 liter/minute, thereby lightly deagglomerating the particles.

[0190] 110 g of methyl hydrogen polysiloxane (tradename: "TSF484", produced by TOSHIBA SILICONE CO., LTD.) were added to the deagglomerated acicular cobalt-coated magnetite particles under the operation of the edge runner. The acicular cobalt-coated magnetite particles were continuously mixed and stirred at a linear load of 30 Kg/cm for 20 minutes.

[0191] Next, 550 g of carbon black fine particles shown in the electron micrograph ($\times 30,000$) of Fig. 2 (particle shape: granular shape; average particle size: 0.022 μm ; geometrical standard deviation value: 1.68; BET specific surface area value: 134 m^2/g ; and blackness (L^* value): 16.6) were added to the acicular cobalt-coated magnetite particles coated with methyl hydrogen polysiloxane for 10 minutes while operating the edge runner. Further, the mixed particles were continuously stirred at a linear load of 30 Kg/cm for 30 minutes to adhere the carbon black fine particles on the coating composed of methyl hydrogen polysiloxane, thereby obtaining black magnetic acicular composite particles.

[0192] The obtained black magnetic acicular composite particles were dried at 80°C for 120 minutes by using a drier to evaporate water or the like which were remained on surfaces of the black magnetic acicular composite particles. As shown in the electron micrograph, the resultant black magnetic acicular composite particles had an average major axis diameter of 0.279 μm , an average minor axis diameter of 0.0332 μm , an aspect ratio of 8.4:1. In addition, the black magnetic acicular composite particles showed a geometrical standard deviation value of 1.38, a BET specific surface area value of 38.9 m^2/g , a blackness (L^* value) of 19.4 and a volume resistivity of $3.6 \times 10^4 \Omega\text{-cm}$. The desorption percentage of the carbon black fine particles from the black magnetic acicular composite particles was 6.0 %. As to the magnetic properties, the coercive force value of the black magnetic acicular composite particles was 676 Oe and the saturation magnetization value was 77.5 emu/g. The coating amount of methyl hydrogen polysiloxane was 0.44 % by weight calculated as Si. Since no independent carbon black fine particles were observed on the electron micrograph, it was determined that a whole amount of the carbon black fine particles were adhered on the coating composed of methyl hydrogen polysiloxane.

<Production of magnetic recording medium: Formation of magnetic recording layer>

[0193] 12 g of the thus obtained black magnetic acicular composite particles, 1.2 g of a polishing agent (AKP-30: trade name, produced by Sumitomo Chemical Co., Ltd.), 0.06 g of carbon black (#3250B, trade name, produced by Mitsubishi Chemical Corp.), a binder resin solution (30 % by weight of vinyl chloride-vinyl acetate copolymer resin having a sodium sulfonate group and 70 % by weight of cyclohexanone) and cyclohexanone were mixed to obtain a mixture (solid content: 78 % by weight). The mixture was further kneaded by a plast-mill for 30 minutes to obtain a kneaded material.

[0194] The thus-obtained kneaded material was charged into a 140 ml-glass bottle together with 95 g of 1.5 mm ϕ glass beads, a binder resin solution (30 % by weight of polyurethane resin having a sodium sulfonate group and 70 % by weight of a solvent (methyl ethyl ketone : toluene = 1 : 1)), cyclohexanone, methyl ethyl ketone and toluene, and the mixture was mixed and dispersed by a paint shaker for 6 hours. Then, the lubricant and hardening agent were added to the mixture, and the resultant mixture was mixed and dispersed by a paint shaker for 15 minutes.

[0195] The thus-obtained magnetic coating composition was the same as Example 1.

[0196] The viscosity of the obtained magnetic coating composition was 2,509 cP.

[0197] The magnetic coating composition obtained was applied to a polyethylene terephthalate film (thickness: 12 μ m) as a non-magnetic base film to a thickness of 45 μ m by an applicator, and the magnetic recording medium obtained was oriented and dried in a magnetic field, and then calendered. The magnetic recording medium was then subjected to a curing reaction at 60°C for 24 hours, and thereafter slit into a width of 0.5 inch, thereby obtaining a magnetic tape. The thickness of the respective magnetic recording layer was 3.4 μ m.

[0198] The coercive force value of the magnetic tape produced by forming a magnetic recording layer on the non-magnetic base film was 736 Oe, the squareness (Br/Bm) thereof was 0.89, the gloss thereof was 178 %, the surface roughness Ra thereof was 6.9 nm, the Young's modulus (relative value) thereof was 138, the linear absorption coefficient thereof was 1.51 μ m⁻¹, and the surface resistivity was 1.8 $\times 10^8 \Omega$ /sq.

Example 3:<Production of black magnetic acicular composite particles>

[0199] 20 kg of acicular cobalt-coated magnetite particles shown in the electron micrograph ($\times 30,000$) of Fig. 1 (cobalt content: 2.21 % by weight based on the weight of the acicular cobalt-coated magnetite particles; Fe²⁺ content: 15.8 % by weight based on the weight of the acicular cobalt-coated magnetite particles; average major axis diameter: 0.278 μ m; average minor axis diameter: 0.0330 μ m; aspect ratio: 8.4:1; geometrical standard deviation value: 1.38; BET specific surface area value: 38.7 m²/g; blackness (L* value): 22.6; volume resistivity: 7.3 $\times 10^7 \Omega$ -cm; coercive force value: 686 Oe; saturation magnetization value: 79.1 emu/g), were deagglomerated in 150 liters of pure water using a stirrer, and further passed through a "TK pipeline homomixer" (tradename, manufactured by Tokushu Kika Kogyo Co., Ltd.) three times, thereby obtaining a slurry containing the acicular cobalt-coated magnetite particles.

[0200] Successively, the obtained slurry containing the acicular cobalt-coated magnetite particles was passed through a transverse-type sand grinder (tradename "MIGHTY MILL MHG-1.5L", manufactured by Inoue Seisakusho Co., Ltd.) five times at an axis-rotating speed of 2,000 rpm, thereby obtaining a slurry in which the acicular cobalt-coated magnetite particles were dispersed.

[0201] The particles in the obtained slurry which remained on a sieve of 325 meshes (mesh size: 44 μ m) was 0 %. The slurry was filtered and washed with water, thereby obtaining a filter cake containing the acicular cobalt-coated magnetite particles. After the obtained filter cake containing the acicular cobalt-coated magnetite particles was dried at 120°C, 11.0 kg of the dried particles were then charged into an edge runner "MPUV-2 Model" (tradename, manufactured by Matsumoto Chuzo Tekkosho Co., Ltd.), and mixed and stirred at 30 Kg/cm for 15 minutes, while introducing nitrogen gas thereinto at a rate of 2 liter/minute, thereby lightly deagglomerating the particles.

[0202] 220 g of tridecafluorooctyl trimethoxysilane (tradename "TSL8257", produced by TOSHIBA SILICONE CO., LTD.) were added to the deagglomerated acicular cobalt-coated magnetite particles under the operation of the edge runner. The acicular cobalt-coated magnetite particles were continuously mixed and stirred at a linear load of 30 Kg/cm for 20 minutes.

[0203] Next, 550 g of carbon black fine particles shown in the electron micrograph ($\times 30,000$) of Fig. 2 (particle shape: granular shape; average particle size: 0.022 μ m; geometrical standard deviation value: 1.68; BET specific surface area value: 134 m²/g; and blackness (L* value): 16.6) were added to the acicular cobalt-coated magnetite particles coated with tridecafluorooctyl trimethoxysilane for 10 minutes while operating the edge runner. Further, the mixed particles were continuously stirred at a linear load of 30 Kg/cm for 30 minutes to adhere the carbon black fine particles on the coating composed of tridecafluorooctyl trimethoxysilane, thereby obtaining black magnetic acicular composite particles.

glass beads, a binder resin solution (30 % by weight of polyurethane resin having a sodium sulfonate group and 70 % by weight of a solvent (methyl ethyl ketone : toluene = 1 : 1)), cyclohexanone, methyl ethyl ketone and toluene, and the mixture was mixed and dispersed by a paint shaker for 6 hours. Then, the lubricant and hardening agent were added to the mixture, and the resultant mixture was mixed and dispersed by a paint shaker for 15 minutes.

[0207] The thus-obtained magnetic coating composition was the same as Example 1.

[0208] The viscosity of the obtained magnetic coating composition was 2,560 cP.

[0209] The magnetic coating composition obtained was applied to a polyethylene terephthalate film (thickness: 12 μm) as a non-magnetic base film to a thickness of 45 μm by an applicator, and the magnetic recording medium obtained was oriented and dried in a magnetic field, and then calendered. The magnetic recording medium was then subjected to a curing reaction at 60°C for 24 hours, and thereafter slit into a width of 0.5 inch, thereby obtaining a magnetic tape. The thickness of the respective magnetic recording layer was 3.5 μm .

[0210] The coercive force value of the magnetic tape produced by forming a magnetic recording layer on the non-magnetic undercoat layer was 735 Oe, the squareness (Br/Bm) thereof was 0.89, the gloss thereof was 176 %, the surface roughness Ra thereof was 7.2 nm, the Young's modulus (relative value) thereof was 138, the linear absorption coefficient thereof was 1.50 μm^{-1} , and the surface resistivity was $1.5 \times 10^8 \Omega/\text{sq}$.

Core particles 1 to 5:

[0211] Various magnetic acicular particles were prepared by known methods. The same procedure as defined in Example 1 was conducted by using the thus magnetic acicular particles, thereby obtaining deagglomerated magnetic acicular particles as core particles.

[0212] Various properties of the thus obtained magnetic acicular particles are shown in Table 1.

Core particles 6:

[0213] The same procedure as defined in Example 1 was conducted by using 20 kg of the deagglomerated acicular cobalt-coated maghemite particles (core particles 1) and 150 liters of water, thereby obtaining a slurry containing the acicular cobalt-coated maghemite particles. The pH value of the obtained redispersed slurry containing the acicular cobalt-coated maghemite particles was adjusted to 10.5 by adding an aqueous sodium hydroxide solution, and then the concentration of the slurry was adjusted to 98 g/liter by adding water thereto. After 150 liters of the-slurry was heated to 60°C, 5,444 ml of a 1.0 mol/liter sodium aluminate solution (equivalent to 1.0 % by weight (calculated as Al) based on the weight of the acicular cobalt-coated maghemite particles) was added to the slurry. After allowing the slurry to stand for 30 minutes, the pH value of the slurry was adjusted to 7.5 by adding an aqueous acetic acid solution. After further allowing the slurry to stand for 30 minutes, the slurry was subjected to filtration, washing with water, drying and pulverization, thereby obtaining the octahedral magnetite particles coated with hydroxides of aluminum.

[0214] Main production conditions are shown in Table 2, and various properties of the obtained acicular cobalt-coated

maghemite particles are shown in Table 3.

Comparative Example 9 to 10:

[0215] The same procedure as defined in the production of the core particles 6 above, was conducted except that kind of core particles, and kind and amount of additives used in the surface treatment were varied, thereby obtaining surface-treated magnetic acicular particles.

[0216] Production conditions are shown in Table 2, and various properties of the obtained surface-treated magnetic acicular composite particles are shown in Table 3.

Example 13 and Comparative Examples 1 to 5:

[0217] The same procedure as defined in Example 1 was conducted except that kind of core particles to be treated, addition or non-addition of an alkoxysilane compound in the coating treatment with the alkoxysilane compound, kind and amount of the alkoxysilane compound added, treating conditions of edge runner in the coating treatment, kind and amount of carbon black fine particles adhered, and treating conditions of edge runner used in the adhering process of the carbon black fine particles, were varied, thereby obtaining black magnetic acicular composite particles. The black magnetic acicular composite particles obtained in Examples 4 to 13 were observed by an electron microscope. As a result, almost no independent carbon black fine particles were recognized. Therefore, it was confirmed that a substantially whole amount of the carbon black fine particles were adhered on the coating composed of organosilane compound produced from the alkoxysilane compound.

[0218] Various properties of the carbon black fine particles A to C are shown in Table 4.

[0219] Main production conditions are shown in Table 5, and various properties of the obtained black magnetic acicular composite particles are shown in Table 6.

[0220] The electron micrograph (x 30,000) of the surface-treated cobalt-coated spindle-shaped maghemite particles as the core particles 7 is shown in Fig. 5. Further, the electron micrograph (x 30,000) of the black magnetic spindle-shaped composite particles obtained in Example 10 by using the surface-treated cobalt-coated spindle-shaped maghemite particles as the core particles 7, is shown in Fig. 6.

[0221] Meanwhile, as a reference, the electron micrograph (x 30,000) of the treated particles obtained by mixing and stirring the surface-treated cobalt-coated spindle-shaped maghemite particles as the core particles 7 and the carbon black fine particles together by an edge runner without coating with methyl triethoxy silane, is shown in Fig. 7. As is shown in the electron micrograph of Fig. 7, it was confirmed that the carbon black fine particles were not adhered to the surfaces of the surface-treated cobalt-coated spindle-shaped maghemite particles, and both the particles were present independently and separately from each other.

Example 14 to 26, Comparative Examples 6 to 20:

<Production of magnetic recording medium>

[0222] The same procedure as defined in Example 1 was conducted except for varying the kind of the magnetic acicular particles, the kind and amount of the carbon black fine particles, thereby producing a magnetic recording medium.

[0223] The main producing conditions and various properties are shown in Tables 7 to 8.

Examples 27 to 56 and Comparative Examples 21 to 29:

[0224] The same procedure as defined in Example 2 was conducted except that kind of core particles to be treated, addition or non-addition of an polysiloxane compound in the coating treatment, kind and amount of the polysiloxane compound added, treating conditions of edge runner in the coating treatment, kind and amount of carbon black fine particles adhered, and treating conditions of edge runner used in the adhering process of the carbon black fine particles, were varied, thereby obtaining black magnetic acicular composite particles. The black magnetic acicular composite particles obtained in Examples 27 to 56 were observed by an electron microscope. As a result, almost no independent carbon black fine particles were recognized. Therefore, it was confirmed that a substantially whole amount of the carbon black fine particles were adhered on the coating composed of polysiloxane.

[0225] Main production conditions are shown in Tables 9, 11 and 13, and various properties of the obtained black magnetic acicular composite particles are shown in Tables 10, 12 and 14.

Example 57 to 95, Comparative Examples 30 to 38:

<Production of magnetic recording medium >

5 [0226] The same procedure as defined in Example 2 was conducted except for varying the kind of the black magnetic acicular composite particles, the kind and amount of the carbon black fine particles, thereby producing a magnetic recording medium.

[0227] The main producing conditions and various properties are shown in Tables 15 to 17.

10 Examples 96 to 105 and Comparative Examples 39 to 41:

[0228] The same procedure as defined in Example 3 was conducted except that kind of core particles to be treated, addition or non-addition of a fluoroalkylsilane compound in the coating treatment with the fluoroalkyl organosilane compound, kind and amount of the fluoroalkylsilane compound added, treating conditions of edge runner in the coating treatment, kind and amount of carbon black fine particles adhered, and treating conditions of edge runner used in the adhering process of the carbon black fine particles, were varied, thereby obtaining black magnetic acicular composite particles. The black magnetic acicular composite particles obtained in Examples 96 to 105 were observed by an electron microscope. As a result, almost no independent carbon black fine particles were recognized. Therefore, it was confirmed that a substantially whole amount of the carbon black fine particles were adhered on the coating composed of fluoroalkyl organosilane compound produced from the fluoroalkylsilane compound.

[0229] Main production conditions are shown in Table 18, and various properties of the obtained black magnetic acicular composite particles are shown in Table 19.

Example 106 to 118, Comparative Examples 42 to 44:

<Production of magnetic recording medium >

[0230] The same procedure as defined in Example 3 was conducted except for varying the kind of the magnetic acicular particles, the kind and amount of the carbon black fine particles, thereby producing a magnetic recording medium.

[0231] The main producing conditions and various properties are shown in Table 20.

Table 1

Core particles	Kind of core particles	Properties of magnetic acicular particles
		Particle shape
Core particles 1	Co-coated maghemite particles (Co content: 2.64 wt. %)	Acicular
Core particles 2	Co-coated maghemite particles (Co content: 4.21 wt. %)	Spindle-shaped
Core particles 3	Co-coated magnetite particles (Co content: 2.21 wt. %) (Fe ²⁺ content: 15.6 wt. %)	Acicular
Core particles 4	Co-coated magnetite particles (Co content: 4.82 wt. %) (Fe ²⁺ content: 13.8 wt. %)	Spindle-shaped
Core particles 5	Magnetic acicular metal particles containing iron as a main component (Al content: 2.74 wt. %) (Co content: 5.61 wt. %)	Spindle-shaped

Table 1 (continued)

Core particles	Properties of magnetic acicular particles		
	Average major axis diameter (μm)	Average minor axis diameter (μm)	Aspect ratio (-)
Core particles 1	0.275	0.0335	8.2:1
Core particles 2	0.211	0.0285	7.4:1
Core particles 3	0.289	0.0361	8.0:1
Core particles 4	0.151	0.0221	6.8:1
Core particles 5	0.127	0.0177	7.2:1

Table 1 (continued)

Core particles	Properties of magnetic acicular particles		
	Geometrical standard deviation value (-)	BET specific surface area value (m ² /g)	Coercive force value (Oe)
Core particles 1	1.40	35.5	689
Core particles 2	1.36	40.8	845
Core particles 3	1.43	31.2	712
Core particles 4	1.44	53.2	913
Core particles 5	1.39	53.4	1,915

Table 1 (continued)

Core particles	Properties of magnetic acicular particles		
	Saturation magnetization value (emu/g)	Volume resistivity ($\Omega \cdot \text{cm}$)	Blackness (L* value) (-)
Core particles 1	76.3	5.2×10^8	24.0
Core particles 2	78.9	3.2×10^8	25.1
Core particles 3	83.1	8.5×10^7	22.5
Core particles 4	81.3	4.8×10^7	22.3
Core particles 5	135.6	1.6×10^7	22.4

Table 2

Core particles	Kind of core particles	Surface-treating process		
		Additives		
		Kind	Calculated as	Amount (wt. %)
Core particles 6	Core particles 1	Sodium aluminate	Al	1.0
Core particles 7	Core particles 2	Water glass #3	SiO ₂	0.75
Core particles 8	Core particles 3	Aluminum sulfate	Al	2.0
		Water glass #3	SiO ₂	0.5
Core particles 9	Core particles 4	Sodium aluminate	Al	0.25
		Colloidal silica	SiO ₂	3.0
Core particles 10	Core particles 5	Water glass #3	SiO ₂	5.0

Table 2 (continued)

Core particles	Surface-treating process		
	Coating material		
	Kinds	Calculated as	Amount (wt. %)
Core particles 6	A	Al	0.98
Core particles 7	S	SiO ₂	0.72
Core particles 8	A	Al	1.93
	S	SiO ₂	0.46
Core particles 9	A	Al	0.24
	S	SiO ₂	2.80
Core particles 10	S	SiO ₂	4.74

Note; A: Hydroxide of aluminum
S: Oxide of silicon

Table 3

Core particles	Properties of surface-treated magnetic acicular particles		
	Average major axis diameter (μm)	Average minor axis diameter (μm)	Aspect ratio (-)
Core particles 6	0.275	0.0335	8.2:1
Core particles 7	0.211	0.0286	7.4:1
Core particles 8	0.289	0.0362	8.0:1
Core particles 9	0.151	0.0221	6.8:1
Core particles 10	0.127	0.0178	7.1:1

Table 3 (continued)

Core particles	Properties of surface-treated magnetic acicular particles		
	Geometrical standard deviation value (-)	BET specific surface area value (m ² /g)	Coercive force value (Oe)
Core particles 6	1.40	35.3	681
Core particles 7	1.36	42.1	832
Core particles 8	1.43	33.3	703
Core particles 9	1.44	54.2	890
Core particles 10	1.39	55.6	1,893

Table 3 (continued)

Core particles	Properties of surface-treated magnetic acicular particles		
	Saturation magnetization value (emu/g)	Volume resistivity ($\Omega \cdot \text{cm}$)	Blackness (L* value) (-)
Core particles 6	75.8	8.6×10^8	24.1
Core particles 7	78.7	4.4×10^8	25.6
Core particles 8	81.9	8.4×10^7	21.8
Core particles 9	79.0	9.1×10^7	22.3
Core particles 10	130.4	3.8×10^7	20.6

Table 4

Kind of carbon black fine particles	Properties of carbon black fine particles		
	Particle shape	Average particle size (μm)	Geometrical standard deviation value (-)
Carbon black A	Granular	0.022	1.78
Carbon black B	Granular	0.015	1.56
Carbon black C	Granular	0.030	2.06

Table 4 (continued)

Kind of carbon black fine particles	Properties of carbon black fine particles	
	BET specific surface area (m^2/g)	Blackness (L^* value) (-)
Carbon black A	133.5	14.6
Carbon black B	265.3	15.2
Carbon black C	84.6	17.0

Table 5

Examples and Comparative Examples	Kind of core particles	Production of black magnetic acicular composite particles	
		Coating with alkoxysilane or silicon compound	
		Additives	
		Kind	Amount added (part by weight)
Example 4	Core particles 1	Methyl triethoxysilane	1.0
Example 5	Core particles 2	Methyl trimethoxysilane	1.5
Example 6	Core particles 3	Dimethyl dimethoxysilane	3.5
Example 7	Core particles 4	Phenyl triethoxysilane	1.0
Example 8	Core particles 5	Isobutyl trimethoxysilane	5.0
Example 9	Core particles 6	Methyl triethoxysilane	2.0
Example 10	Core particles 7	Methyl trimethoxysilane	1.0
Example 11	Core particles 8	Dimethyl dimethoxysilane	2.0
Example 12	Core particles 9	Phenyl triethoxysilane	4.5
Example 13	Core particles 10	Isobutyl trimethoxysilane	3.0
Comparative Example 1	Core particles 1	-	-
Comparative Example 2	Core particles 1	Methyl triethoxysilane	1.0
Comparative Example 3	Core particles 4	Dimethyl dimethoxysilane	0.5
Comparative Example 4	Core particles 4	Methyl triethoxysilane	0.005
Comparative Example 5	Core particles 1	γ -aminopropyl triethoxysilane	1.0

Table 5 (continued)

Examples and Comparative Examples	Production of black magnetic acicular composite particles		
	Coating with alkoxysilane or silicon compound		
	Edge runner treatment		Coating amount (calculated as Si) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 4	30	30	0.16
Example 5	45	20	0.30
Example 6	30	20	0.79
Example 7	30	20	0.12
Example 8	15	20	0.75
Example 9	45	20	0.31
Example 10	60	30	0.20
Example 11	25	20	0.46
Example 12	30	20	0.50
Example 13	15	20	0.46
Comparative Example 1	-	-	-
Comparative Example 2	30	20	0.16
Comparative Example 3	30	20	0.12
Comparative Example 4	30	20	7×10^{-4}
Comparative Example 5	30	20	0.13

Table 5 (continued)

Examples and Comparative Examples	Production of black magnetic acicular composite particles	
	Adhesion of carbon black	
	Carbon black	
	Kind	Amount added (part by weight)
Example 4	A	5.0
Example 5	A	3.0
Example 6	B	1.0
Example 7	B	1.5
Example 8	C	2.0
Example 9	A	5.0
Example 10	A	3.0
Example 11	B	1.0
Example 12	B	2.0
Example 13	C	1.0
Comparative Example 1	A	2.0
Comparative Example 2	-	-
Comparative Example 3	A	0.01
Comparative Example 4	B	2.0
Comparative Example 5	C	2.0

Table 5 (continued)

Examples and Comparative Examples	Production of black magnetic acicular composite particles		
	Adhesion of carbon black		
	Edge runner treatment		Amount adhered (calculated as C) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 4	30	30	4.75
Example 5	45	20	2.82
Example 6	60	30	0.97
Example 7	30	20	1.45
Example 8	15	20	1.89
Example 9	30	20	4.76
Example 10	20	20	2.89
Example 11	60	20	0.99
Example 12	45	20	1.96
Example 13	15	20	0.98
Comparative Example 1	30	20	1.95
Comparative Example 2	-	-	-
Comparative Example 3	30	20	0.009
Comparative Example 4	30	20	1.96
Comparative Example 5	30	20	1.95

Table 6

Examples and Comparative Examples	Properties of black magnetic acicular composite particles			
	Average major axis diameter (μm)	Average minor axis diameter (μm)	Aspect ratio (-)	Geometrical standard deviation value (-)
Example 4	0.276	0.0336	8.2:1	1.40
Example 5	0.212	0.0286	7.4:1	1.36
Example 6	0.290	0.0363	8.0:1	1.43
Example 7	0.153	0.0224	6.8:1	1.44
Example 8	0.129	0.0178	7.2:1	1.39
Example 9	0.277	0.0337	8.2:1	1.40
Example 10	0.212	0.0287	7.4:1	1.36
Example 11	0.291	0.0363	8.0:1	1.43
Example 12	0.152	0.0222	6.8:1	1.44
Example 13	0.128	0.0180	7.1:1	1.39
Comparative Example 1	0.275	0.0336	8.2:1	-
Comparative Example 2	0.275	0.0335	8.2:1	1.40
Comparative Example 3	0.151	0.0221	6.8:1	-
Comparative Example 4	0.152	0.0223	6.8:1	-
Comparative Example 5	0.275	0.0337	8.2:1	-

Table 6 (continued)

Examples and Comparative Examples	Properties of black magnetic acicular composite particles		
	BET specific surface area value (m ² /g)	Coercive force value (Oe)	Saturation magnetization value (emu/g)
Example 4	29.8	683	74.2
Example 5	35.4	832	76.5
Example 6	26.5	698	80.6
Example 7	45.6	905	79.2
Example 8	51.3	1,894	133.8
Example 9	28.9	670	73.2
Example 10	36.0	821	76.5
Example 11	27.1	689	78.6
Example 12	46.2	881	77.1
Example 13	46.8	1,889	129.5
Comparative Example 1	36.3	679	75.9
Comparative Example 2	33.5	682	76.0
Comparative Example 3	48.1	898	81.0
Comparative Example 4	58.6	904	80.1
Comparative Example 5	32.4	680	75.4

Table 6 (continued)

Examples and Comparative Examples	Properties of black magnetic acicular composite particles		
	Volume resistivity ($\Omega \cdot \text{cm}$)	Blackness (L^* value) (-)	Carbon black desorption percentage (%)
Example 4	6.6×10^4	18.9	8.1
Example 5	2.6×10^5	19.6	7.6
Example 6	9.6×10^5	20.4	8.6
Example 7	8.3×10^5	19.9	9.1
Example 8	5.5×10^5	19.4	7.2
Example 9	1.4×10^4	18.6	4.8
Example 10	8.8×10^4	20.2	3.2
Example 11	6.8×10^5	18.9	4.6
Example 12	1.8×10^5	18.6	2.6
Example 13	5.1×10^5	19.0	4.1
Comparative Example 1	5.6×10^7	23.5	61.6
Comparative Example 2	5.6×10^8	24.6	-
Comparative Example 3	6.4×10^7	22.4	-
Comparative Example 4	7.6×10^6	22.0	41.2
Comparative Example 5	2.6×10^7	23.5	55.8

Table 7

Examples	Production of magnetic coating composition		
	Kind of magnetic acicular particles	Weight ratio of particles to resin (-)	Amount of carbon black added (ratio to magnetic particles) (part by weight)
Example 14	Example 4	5.0:1	0.50
Example 15	Example 5	5.0:1	0.50
Example 16	Example 6	5.0:1	0.50
Example 17	Example 7	5.0:1	0.50
Example 18	Example 8	5.0:1	0.50
Example 19	Example 9	5.0:1	0.50
Example 20	Example 10	5.0:1	0.50
Example 21	Example 11	5.0:1	0.50
Example 22	Example 12	5.0:1	0.50
Example 23	Example 13	5.0:1	0.50
Example 24	Example 4	5.0:1	0.00
Example 25	Example 6	5.0:1	2.50
Example 26	Example 8	5.0:1	1.50

Table 7 (continued)

Examples	Properties of coating composition	Properties of magnetic recording medium	
	Viscosity (cP)	Thickness of magnetic layer (μm)	Coercive force value (Oe)
Example 14	2,304	3.3	732
Example 15	2,816	3.5	896
Example 16	3,072	3.4	747
Example 17	2,944	3.5	954
Example 18	5,120	4.3	1,954
Example 19	2,381	3.3	728
Example 20	2,816	3.3	890
Example 21	2,765	3.4	741
Example 22	2,688	3.5	950
Example 23	4,864	3.8	1,939
Example 24	2,048	3.5	732
Example 25	3,840	3.5	742
Example 26	5,632	3.6	1,946

Table 7 (continued)

Examples	Properties of magnetic recording medium		
	Br/Bm (-)	Gloss (%)	Surface roughness Ra (nm)
Example 14	0.89	171	8.4
Example 15	0.89	174	6.8
Example 16	0.88	171	8.6
Example 17	0.88	173	7.6
Example 18	0.88	231	8.0
Example 19	0.90	175	7.6
Example 20	0.91	176	6.4
Example 21	0.89	171	8.6
Example 22	0.88	174	7.2
Example 23	0.89	235	7.2
Example 24	0.89	175	8.0
Example 25	0.88	167	9.7
Example 26	0.88	213	8.8

Table 7 (continued)

Examples	Properties of magnetic recording medium		
	Young's modulus (relative value)	Linear absorption (μm^{-1})	Surface resistivity (Ω/sq)
Example 14	138	1.44	2.3×10^8
Example 15	134	1.35	5.4×10^8
Example 16	141	1.52	8.7×10^8
Example 17	134	1.45	1.9×10^9
Example 18	136	1.48	7.1×10^8
Example 19	139	1.43	7.8×10^8
Example 20	136	1.36	6.3×10^8
Example 21	143	1.49	1.4×10^8
Example 22	135	1.46	2.5×10^9
Example 23	135	1.50	1.0×10^9
Example 24	138	1.36	1.2×10^9
Example 25	136	1.64	1.1×10^8
Example 26	133	1.58	2.6×10^8

Table 8

Comparative Examples	Production of magnetic coating composition		
	Kind of magnetic acicular particles	Weight ratio of particles to resin (-)	Amount of carbon black added (ratio to magnetic particles) (part by weight)
Comparative Example 6	Core particles 1	5.0:1	0.50
Comparative Example 7	Core particles 2	5.0:1	0.50
Comparative Example 8	Core particles 3	5.0:1	0.50
Comparative Example 9	Core particles 4	5.0:1	0.50
Comparative Example 10	Core particles 5	5.0:1	0.50
Comparative Example 11	Comparative Example 1	5.0:1	0.50
Comparative Example 12	Comparative Example 2	5.0:1	0.50
Comparative Example 13	Comparative Example 3	5.0:1	0.50
Comparative Example 14	Comparative Example 4	5.0:1	0.50
Comparative Example 15	Comparative Example 5	5.0:1	0.50
Comparative Example 16	Core particles 1	5.0:1	10.00
Comparative Example 17	Core particles 3	5.0:1	10.00
Comparative Example 18	Core particles 3	5.0:1	5.50
Comparative Example 19	Core particles 5	5.0:1	10.00
Comparative Example 20	Core particles 5	5.0:1	5.50

Table 8 (continued)

Comparative Examples	Properties of coating composition	Properties of magnetic recording medium	
	Viscosity (cP)	Thickness of magnetic layer (μm)	Coercive force value (Oe)
Comparative Example 6	2,560	3.5	730
Comparative Example 7	2,688	3.4	899
Comparative Example 8	2,944	3.3	745
Comparative Example 9	3,328	3.5	950
Comparative Example 10	5,376	3.5	1,940
Comparative Example 11	4,096	3.4	730
Comparative Example 12	2,381	3.4	735
Comparative Example 13	2,739	3.3	941
Comparative Example 14	4,352	3.5	945
Comparative Example 15	2,816	3.4	731
Comparative Example 16	5,888	3.7	725
Comparative Example 17	6,477	3.7	739
Comparative Example 18	4,122	3.5	742
Comparative Example 19	12,902	3.9	1,932
Comparative Example 20	5,376	3.6	1,936

Table 8 (continued)

Comparative Examples	Properties of magnetic recording medium		
	Br/Bm (-)	Gloss (%)	Surface roughness Ra (nm)
Comparative Example 6	0.88	168	10.2
Comparative Example 7	0.88	167	10.2
Comparative Example 8	0.87	163	10.8
Comparative Example 9	0.87	168	11.2
Comparative Example 10	0.87	208	13.8
Comparative Example 11	0.83	156	15.6
Comparative Example 12	0.86	169	11.2
Comparative Example 13	0.85	165	10.2
Comparative Example 14	0.84	161	14.8
Comparative Example 15	0.84	159	13.1
Comparative Example 16	0.82	131	21.6
Comparative Example 17	0.82	125	23.6
Comparative Example 18	0.85	153	14.5
Comparative Example 19	0.74	136	36.8
Comparative Example 20	0.79	185	16.7

Table 8 (continued)

Comparative Examples	Properties of magnetic recording medium		
	Young's modulus (relative value)	Linear absorption (μm^{-1})	Surface resistivity (Ω/sq)
Comparative Example 6	134	0.64	6.2×10^{12}
Comparative Example 7	133	0.48	2.2×10^{13}
Comparative Example 8	133	1.05	8.1×10^{11}
Comparative Example 9	134	0.89	3.6×10^{11}
Comparative Example 10	128	1.08	4.7×10^{11}
Comparative Example 11	121	1.15	1.3×10^{11}
Comparative Example 12	126	0.64	9.7×10^{11}
Comparative Example 13	132	0.93	9.1×10^{11}
Comparative Example 14	128	1.19	5.6×10^{10}
Comparative Example 15	122	1.16	8.0×10^{11}
Comparative Example 16	117	1.38	5.3×10^9
Comparative Example 17	112	1.44	1.1×10^9
Comparative Example 18	127	1.14	2.2×10^{10}
Comparative Example 19	105	1.39	3.7×10^9
Comparative Example 20	114	1.15	1.7×10^{10}

Table 9

Examples and Comparative Examples	Kind of core particles	Production of black magnetic acicular composite particles	
		Coating with polysiloxane	
		Additives	
		Kind	Amount added (part by weight)
Example 27	Core particles 1	TSF484	1.0
Example 28	Core particles 2	TSF484	3.0
Example 29	Core particles 3	KF99	2.0
Example 30	Core particles 4	L-9000	0.5
Example 31	Core particles 5	TSF484/TSF451	0.4/0.1
Example 32	Core particles 6	TSF484/L-45	0.5/1.5
Example 33	Core particles 7	TSF451	2.0
Example 34	Core particles 8	TSF484	1.0
Example 35	Core particles 9	TSF484	1.5
Example 36	Core particles 10	KF99	1.0
Comparative Example 21	Core particles 1	TSF484	1.0
Comparative Example 22	Core particles 4	TSF484	0.5
Comparative Example 23	Core particles 4	TSF484	0.005

Table 9 (continued)

Examples and Comparative Examples	Production of black magnetic acicular composite particles		
	Coating with polysiloxane		
	Edge runner treatment		Coating amount (calculated as Si) (wt. %)
	Linear load (kg/cm)	Time (min)	
Example 27	60	30	0.43
Example 28	30	60	1.23
Example 29	45	20	0.87
Example 30	75	30	0.21
Example 31	30	30	0.22
Example 32	60	45	0.85
Example 33	60	20	0.86
Example 34	45	30	0.44
Example 35	45	45	0.63
Example 36	60	20	0.42
Comparative Example 21	30	20	0.43
Comparative Example 22	30	20	0.22
Comparative Example 23	30	20	2×10^{-3}

Table 9 (continued)

Examples and Comparative Examples	Production of black magnetic acicular composite particles	
	Adhesion of carbon black	
	Carbon black	
	Kind	Amount added (part by weight)
Example 27	A	10.0
Example 28	A	2.5
Example 29	B	5.0
Example 30	B	7.5
Example 31	C	10.0
Example 32	A	3.0
Example 33	A	7.5
Example 34	B	5.0
Example 35	B	10.0
Example 36	C	10.0
Comparative Example 21	-	-
Comparative Example 22	A	0.01
Comparative Example 23	B	2.0

Table 9 (continued)

Examples and Comparative Examples	Production of black magnetic acicular composite particles		
	Adhesion of carbon black		
	Edge runner treatment		Amount adhered (calculated as C) (wt. %)
	Linear load (kg/cm)	Time (min)	
Example 27	45	30	9.08
Example 28	30	60	2.43
Example 29	60	30	4.76
Example 30	45	30	6.96
Example 31	30	45	9.07
Example 32	60	45	2.91
Example 33	45	45	6.95
Example 34	75	60	4.75
Example 35	60	60	9.06
Example 36	30	30	9.07
Comparative Example 21	-	-	-
Comparative Example 22	30	20	0.009
Comparative Example 23	30	20	1.96

Table 10

Examples and Comparative Examples	Properties of black magnetic acicular composite particles			
	Average major axis diameter (μm)	Average minor axis diameter (μm)	Aspect ratio (-)	Geometrical standard deviation value (-)
Example 27	0.276	0.0335	8.2:1	1.40
Example 28	0.212	0.0286	7.4:1	1.36
Example 29	0.290	0.0364	8.0:1	1.43
Example 30	0.153	0.0223	6.9:1	1.44
Example 31	0.129	0.0178	7.2:1	1.39
Example 32	0.278	0.0336	8.3:1	1.40
Example 33	0.211	0.0288	7.3:1	1.36
Example 34	0.290	0.0365	7.9:1	1.43
Example 35	0.153	0.0222	6.9:1	1.44
Example 36	0.128	0.0180	7.1:1	1.39
Comparative Example 21	0.275	0.0336	8.2:1	1.40
Comparative Example 22	0.152	0.0222	6.8:1	-
Comparative Example 23	0.152	0.0222	6.8:1	-

Table 10 (continued)

Examples and Comparative Examples	Properties of black magnetic acicular composite particles		
	BET specific surface area value (m ² /g)	Coercive force value (Oe)	Saturation magnetization value (emu/g)
Example 27	35.4	685	74.3
Example 28	40.3	833	77.1
Example 29	31.8	700	81.2
Example 30	50.2	910	79.0
Example 31	57.6	1,895	132.1
Example 32	34.1	673	73.6
Example 33	41.8	824	76.8
Example 34	32.2	694	80.1
Example 35	51.8	888	80.0
Example 36	51.8	1,896	128.9
Comparative Example 21	38.4	683	76.1
Comparative Example 22	52.8	900	80.9
Comparative Example 23	62.1	906	80.3

Table 10 (continued)

Examples and Comparative Examples	Properties of black magnetic acicular composite particles		
	Volume resistivity ($\Omega \cdot \text{cm}$)	Blackness (L* value) (-)	Carbon black desorption percentage (%)
Example 27	5.2×10^4	18.8	7.8
Example 28	3.1×10^5	20.0	8.3
Example 29	8.6×10^5	20.3	9.1
Example 30	6.3×10^5	20.1	8.6
Example 31	5.1×10^5	19.2	7.1
Example 32	2.1×10^4	20.8	4.8
Example 33	6.6×10^4	20.2	3.6
Example 34	7.1×10^5	18.8	2.6
Example 35	1.4×10^5	18.8	3.4
Example 36	3.8×10^5	19.1	5.2
Comparative Example 21	6.5×10^8	24.5	-
Comparative Example 22	8.1×10^7	23.1	-
Comparative Example 23	1.2×10^7	22.2	46.6

Table 11

Examples and Comparative Examples	Kind of core particles	Production of black magnetic acicular composite particles	
		Coating with modified polysiloxane	
		Additives	
		Kind	Amount added (part by weight)
Example 37	Core particles 1	BYK-080	1.0
Example 38	Core particles 2	BYK-080	0.5
Example 39	Core particles 3	BYK-310	2.0
Example 40	Core particles 4	BYK-322	3.0
Example 41	Core particles 5	TSF4446	1.0
Example 42	Core particles 6	TSF4460	1.5
Example 43	Core particles 7	YF3965	1.0
Example 44	Core particles 8	BYK-080	1.0
Example 45	Core particles 9	BYK-080	3.0
Example 46	Core particles 10	BYK-310	1.0
Comparative Example 24	Core particles 1	BYK-080	1.0
Comparative Example 25	Core particles 4	BYK-080	0.5
Comparative Example 26	Core particles 4	BYK-080	0.005

Table 11 (continued)

Examples and Comparative Examples	Production of black magnetic acicular composite particles		
	Coating with modified polysiloxane		
	Edge runner treatment		Coating amount (calculated as Si) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 37	60	30	0.17
Example 38	30	20	0.08
Example 39	60	30	0.33
Example 40	45	45	0.56
Example 41	60	30	0.17
Example 42	45	30	0.25
Example 43	60	20	0.16
Example 44	30	30	0.18
Example 45	60	45	0.53
Example 46	60	30	0.16
Comparative Example 24	30	20	0.17
Comparative Example 25	30	20	0.08
Comparative Example 26	30	20	8×10^{-4}

Table 11 (continued)

Examples and Comparative Examples	Production of black magnetic acicular composite particles	
	Adhesion of carbon black	
	Carbon black	
	Kind	Amount added (part by weight)
Example 37	A	10.0
Example 38	A	5.0
Example 39	B	7.5
Example 40	B	10.0
Example 41	C	15.0
Example 42	A	10.0
Example 43	A	10.0
Example 44	B	7.5
Example 45	B	10.0
Example 46	C	15.0
Comparative Example 24	-	-
Comparative Example 25	A	0.01
Comparative Example 26	B	2.0

Table 11 (continued)

Examples and Comparative Examples	Production of black magnetic acicular composite particles		
	Adhesion of carbon black		
	Edge runner treatment		Amount adhered (calculated as C) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 37	60	30	9.08
Example 38	30	45	4.76
Example 39	60	30	6.96
Example 40	60	30	9.07
Example 41	60	20	13.03
Example 42	45	45	9.08
Example 43	60	30	9.08
Example 44	30	30	6.95
Example 45	45	30	9.06
Example 46	45	30	13.00
Comparative Example 24	-	-	-
Comparative Example 25	30	20	0.009
Comparative Example 26	30	20	1.95

Table 12

Examples and Comparative Examples	Properties of black magnetic acicular composite particles			
	Average major axis diameter (μm)	Average minor axis diameter (μm)	Aspect ratio (-)	Geometrical standard deviation value (-)
Example 37	0.276	0.0336	8.2:1	1.40
Example 38	0.212	0.0286	7.4:1	1.36
Example 39	0.290	0.0363	8.0:1	1.43
Example 40	0.152	0.0223	6.8:1	1.44
Example 41	0.130	0.0178	7.3:1	1.39
Example 42	0.278	0.0336	8.3:1	1.40
Example 43	0.213	0.0287	7.4:1	1.36
Example 44	0.290	0.0365	7.9:1	1.43
Example 45	0.152	0.0223	6.8:1	1.44
Example 46	0.128	0.0179	7.2:1	1.39
Comparative Example 24	0.276	0.0336	8.2:1	1.40
Comparative Example 25	0.152	0.0222	6.8:1	-
Comparative Example 26	0.152	0.0221	6.9:1	-

Table 12 (continued)

Examples and Comparative Examples	Properties of black magnetic acicular composite particles		
	BET specific surface area value (m ² /g)	Coercive force value (Oe)	Saturation magnetization value (emu/g)
Example 37	36.0	683	74.1
Example 38	40.2	830	76.9
Example 39	31.9	701	81.0
Example 40	50.3	912	79.5
Example 41	57.2	1,898	132.0
Example 42	34.3	671	73.5
Example 43	41.9	821	76.5
Example 44	32.3	693	81.0
Example 45	51.9	885	80.8
Example 46	51.8	1,890	128.3
Comparative Example 24	38.6	684	76.1
Comparative Example 25	52.4	898	80.8
Comparative Example 26	62.3	905	80.4

Table 12 (continued)

Examples and Comparative Examples	Properties of black magnetic acicular composite particles		
	Volume resistivity ($\Omega \cdot \text{cm}$)	Blackness (L^* value) (-)	Carbon black desorption percentage (%)
Example 37	3.6×10^4	18.6	6.8
Example 38	3.1×10^5	19.6	6.1
Example 39	8.4×10^5	19.2	7.3
Example 40	6.4×10^5	19.6	7.5
Example 41	5.1×10^5	19.0	8.1
Example 42	1.3×10^4	19.8	3.6
Example 43	6.5×10^4	19.6	2.1
Example 44	4.6×10^5	18.4	3.1
Example 45	3.6×10^5	18.2	2.1
Example 46	4.2×10^5	18.6	3.8
Comparative Example 24	4.3×10^8	24.4	-
Comparative Example 25	6.9×10^7	23.8	-
Comparative Example 26	2.2×10^7	23.1	43.3

Table 13

Examples and Comparative Examples	Kind of core particles	Production of black magnetic acicular composite particles	
		Coating with terminal-modified polysiloxane	
		Additives	
		Kind	Amount added (part by weight)
Example 47	Core particles 1	TSF4770	2.0
Example 48	Core particles 2	TSF4770	1.0
Example 49	Core particles 3	TSF4751	0.5
Example 50	Core particles 4	TSF4751	3.0
Example 51	Core particles 5	XF3905	5.0
Example 52	Core particles 6	XF3905	1.5
Example 53	Core particles 7	YF3804	2.0
Example 54	Core particles 8	TSF4770	1.5
Example 55	Core particles 9	TSF4770	1.0
Example 56	Core particles 10	TSF4751	1.0
Comparative Example 27	Core particles 1	TSF4770	1.0
Comparative Example 28	Core particles 4	TSF4770	0.5
Comparative Example 29	Core particles 4	TSF4770	0.005

Table 13 (continued)

Examples and Comparative Examples	Production of black magnetic acicular composite particles		
	Coating with terminal-modified polysiloxane		
	Edge runner treatment		Coating amount (calculated as Si) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 47	30	30	0.68
Example 48	60	20	0.33
Example 49	60	20	0.17
Example 50	45	45	1.05
Example 51	30	30	1.71
Example 52	60	30	0.50
Example 53	60	20	0.39
Example 54	45	45	0.50
Example 55	30	30	0.33
Example 56	60	30	0.35
Comparative Example 27	30	20	0.34
Comparative Example 28	30	20	0.16
Comparative Example 29	30	20	1×10^{-3}

Table 13 (continued)

Examples and Comparative Examples	Production of black magnetic acicular composite particles	
	Adhesion of carbon black	
	Carbon black	
	Kind	Amount added (part by weight)
Example 47	A	10.0
Example 48	A	5.0
Example 49	B	10.0
Example 50	B	10.0
Example 51	C	15.0
Example 52	A	15.0
Example 53	A	10.0
Example 54	B	7.5
Example 55	B	10.0
Example 56	C	15.0
Comparative Example 27	-	-
Comparative Example 28	A	0.01
Comparative Example 29	B	2.0

Table 13 (continued)

Examples and Comparative Examples	Production of black magnetic acicular composite particles		
	Adhesion of carbon black		
	Edge runner treatment		Amount adhered (calculated as C) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 47	60	60	9.08
Example 48	45	30	4.75
Example 49	30	30	9.07
Example 50	60	60	9.07
Example 51	45	60	13.02
Example 52	45	30	13.00
Example 53	30	30	9.09
Example 54	30	60	6.95
Example 55	60	60	9.06
Example 56	60	30	13.03
Comparative Example 27	-	-	-
Comparative Example 28	30	20	0.009
Comparative Example 29	30	20	1.95

Table 14

Examples and Comparative Examples	Properties of black magnetic acicular composite particles			
	Average major axis diameter (μm)	Average minor axis diameter (μm)	Aspect ratio (-)	Geometrical standard deviation value (-)
Example 47	0.276	0.0335	8.2:1	1.41
Example 48	0.212	0.0286	7.4:1	1.36
Example 49	0.290	0.0363	8.0:1	1.42
Example 50	0.153	0.0223	6.9:1	1.44
Example 51	0.131	0.0179	7.3:1	1.39
Example 52	0.279	0.0336	8.3:1	1.41
Example 53	0.212	0.0287	7.4:1	1.36
Example 54	0.291	0.0364	8.0:1	1.43
Example 55	0.153	0.0224	6.8:1	1.44
Example 56	0.128	0.0180	7.1:1	1.39
Comparative Example 27	0.275	0.0335	8.2:1	1.40
Comparative Example 28	0.151	0.0222	6.8:1	-
Comparative Example 29	0.152	0.0221	6.9:1	-

Table 14 (continued)

Examples and Comparative Examples	Properties of black magnetic acicular composite particles		
	BET specific surface area value (m ² /g)	Coercive force value (Oe)	Saturation magnetization value (emu/g)
Example 47	35.8	682	74.0
Example 48	39.9	831	76.4
Example 49	31.9	698	80.6
Example 50	50.5	913	78.9
Example 51	56.6	1,901	131.6
Example 52	34.5	672	73.1
Example 53	42.1	823	76.3
Example 54	32.5	695	81.6
Example 55	52.1	886	79.5
Example 56	51.9	1,982	127.2
Comparative Example 27	38.6	683	76.3
Comparative Example 28	52.5	899	81.0
Comparative Example 29	62.1	903	80.9

Table 14 (continued)

Examples and Comparative Examples	Properties of black magnetic acicular composite particles		
	Volume resistivity ($\Omega \cdot \text{cm}$)	Blackness (L* value) (-)	Carbon black desorption percentage (%)
Example 47	5.1×10^4	18.5	5.6
Example 48	3.2×10^5	19.6	6.8
Example 49	8.3×10^5	19.0	9.2
Example 50	6.1×10^5	19.5	8.3
Example 51	2.8×10^5	18.8	6.9
Example 52	3.6×10^4	19.5	3.2
Example 53	9.2×10^4	19.3	4.1
Example 54	1.8×10^5	18.1	3.8
Example 55	6.4×10^5	18.2	2.9
Example 56	5.6×10^5	18.0	3.6
Comparative Example 27	3.2×10^8	24.2	-
Comparative Example 28	7.1×10^7	24.0	-
Comparative Example 29	1.5×10^7	23.4	45.5

Table 15

Examples and Comparative Examples	Production of magnetic coating composition		
	Kind of magnetic acicular particles	Weight ratio of particles to resin (-)	Amount of carbon black added (ratio to magnetic particles) (part by weight)
Example 57	Example 27	5.0:1	0.50
Example 58	Example 28	5.0:1	0.50
Example 59	Example 29	5.0:1	0.50
Example 60	Example 30	5.0:1	0.50
Example 61	Example 31	5.0:1	0.50
Example 62	Example 32	5.0:1	0.50
Example 63	Example 33	5.0:1	0.50
Example 64	Example 34	5.0:1	0.50
Example 65	Example 35	5.0:1	0.50
Example 66	Example 36	5.0:1	0.50
Example 67	Example 27	5.0:1	0.00
Example 68	Example 29	5.0:1	2.50
Example 69	Example 31	5.0:1	1.50
Comparative Example 30	Comparative Example 21	5.0:1	0.50
Comparative Example 31	Comparative Example 22	5.0:1	0.50
Comparative Example 32	Comparative Example 23	5.0:1	0.50

Table 15 (continued)

Examples and Comparative Examples	Properties of coating composition	Properties of magnetic recording medium	
	Viscosity (cP)	Thickness of magnetic layer (μm)	Coercive force value (Oe)
Example 57	2,432	3.3	731
Example 58	2,534	3.5	893
Example 59	2,688	3.4	745
Example 60	2,611	3.3	959
Example 61	5,376	4.0	1,968
Example 62	2,406	3.5	736
Example 63	2,944	3.4	893
Example 64	2,790	3.5	747
Example 65	3,302	3.4	958
Example 66	5,146	3.9	1,952
Example 67	2,308	3.3	733
Example 68	3,891	3.4	742
Example 69	5,018	3.5	1,952
Comparative Example 30	3,610	3.6	735
Comparative Example 31	3,354	3.5	939
Comparative Example 32	3,098	3.6	941

Table 15 (continued)

Examples and Comparative Examples	Properties of magnetic recording medium		
	Br/Bm (-)	Gloss (%)	Surface roughness Ra (nm)
Example 57	0.89	172	8.2
Example 58	0.88	175	6.9
Example 59	0.89	170	8.4
Example 60	0.89	173	7.9
Example 61	0.88	230	7.9
Example 62	0.89	170	7.8
Example 63	0.90	171	8.1
Example 64	0.90	173	8.0
Example 65	0.89	175	7.6
Example 66	0.88	231	7.1
Example 67	0.89	176	7.6
Example 68	0.89	170	8.0
Example 69	0.88	232	7.8
Comparative Example 30	0.85	164	12.1
Comparative Example 31	0.85	163	11.8
Comparative Example 32	0.83	160	13.6

Table 15 (continued)

Examples and Comparative Examples	Properties of magnetic recording medium		
	Young's modulus (relative value)	Linear absorption (μm^{-1})	Surface resistivity (Ω/sq)
Example 57	138	1.44	1.6×10^8
Example 58	135	1.36	2.6×10^8
Example 59	140	1.53	6.8×10^8
Example 60	135	1.46	3.1×10^9
Example 61	135	1.50	2.1×10^8
Example 62	136	1.42	4.6×10^8
Example 63	140	1.38	3.2×10^8
Example 64	137	1.47	1.9×10^8
Example 65	143	1.43	2.8×10^9
Example 66	135	1.51	1.1×10^9
Example 67	136	1.36	1.3×10^9
Example 68	136	1.51	1.9×10^8
Example 69	136	1.48	4.2×10^8
Comparative Example 30	125	0.68	8.8×10^{11}
Comparative Example 31	128	0.98	9.0×10^{11}
Comparative Example 32	127	1.16	5.3×10^{10}

Table 16

Examples and Comparative Examples	Production of magnetic coating composition		
	Kind of magnetic acicular particles	Weight ratio of particles to resin (-)	Amount of carbon black added (ratio to magnetic particles) (part by weight)
Example 70	Example 37	5.0:1	0.50
Example 71	Example 38	5.0:1	0.50
Example 72	Example 39	5.0:1	0.50
Example 73	Example 40	5.0:1	0.50
Example 74	Example 41	5.0:1	0.50
Example 75	Example 42	5.0:1	0.50
Example 76	Example 43	5.0:1	0.50
Example 77	Example 44	5.0:1	0.50
Example 78	Example 45	5.0:1	0.50
Example 79	Example 46	5.0:1	0.50
Example 80	Example 37	5.0:1	0.00
Example 81	Example 39	5.0:1	2.50
Example 82	Example 41	5.0:1	1.50
Comparative Example 33	Comparative Example 24	5.0:1	0.50
Comparative Example 34	Comparative Example 25	5.0:1	0.50
Comparative Example 35	Comparative Example 26	5.0:1	0.50

Table 16 (continued)

Examples and Comparative Examples	Properties of coating composition	Properties of magnetic recording medium	
	Viscosity (cP)	Thickness of magnetic layer (μm)	Coercive force value (Oe)
Example 70	2,688	3.5	733
Example 71	2,764	3.4	896
Example 72	3,021	3.3	743
Example 73	2,944	3.4	965
Example 74	5,888	3.8	1,971
Example 75	3,302	3.3	738
Example 76	3,046	3.3	891
Example 77	2,790	3.4	750
Example 78	2,560	3.1	961
Example 79	5,171	3.9	1,954
Example 80	2,586	3.2	733
Example 81	3,610	3.3	743
Example 82	3,098	3.5	1,962
Comparative Example 33	3,046	3.6	732
Comparative Example 34	3,302	3.5	932
Comparative Example 35	2,944	3.5	940

Table 16 (continued)

Examples and Comparative Examples	Properties of magnetic recording medium		
	Br/Bm (-)	Gloss (%)	Surface roughness Ra (nm)
Example 70	0.88	173	8.0
Example 71	0.89	176	7.4
Example 72	0.88	171	8.2
Example 73	0.89	174	7.4
Example 74	0.88	235	7.4
Example 75	0.89	173	7.9
Example 76	0.89	172	8.2
Example 77	0.89	175	7.5
Example 78	0.89	175	7.5
Example 79	0.89	235	7.8
Example 80	0.89	175	6.8
Example 81	0.88	171	7.5
Example 82	0.89	233	7.6
Comparative Example 33	0.85	162	12.3
Comparative Example 34	0.84	160	12.3
Comparative Example 35	0.83	160	13.8

Table 16 (continued)

Examples and Comparative Examples	Properties of magnetic recording medium		
	Young's modulus (relative value)	Linear absorption (μm^{-1})	Surface resistivity (Ω/sq)
Example 70	137	1.45	3.2×10^8
Example 71	135	1.38	4.6×10^8
Example 72	139	1.52	7.9×10^8
Example 73	136	1.48	2.1×10^9
Example 74	135	1.49	1.8×10^8
Example 75	136	1.43	6.5×10^8
Example 76	140	1.36	7.1×10^8
Example 77	137	1.51	4.3×10^8
Example 78	142	1.50	1.3×10^9
Example 79	136	1.54	1.2×10^9
Example 80	136	1.46	1.3×10^9
Example 81	137	1.53	4.1×10^8
Example 82	136	1.48	5.2×10^8
Comparative Example 33	124	0.66	8.6×10^{11}
Comparative Example 34	127	0.93	8.8×10^{11}
Comparative Example 35	126	1.12	4.9×10^{10}

Table 17

Examples and Comparative Examples	Production of magnetic coating composition		
	Kind of magnetic acicular particles	Weight ratio of particles to resin (-)	Amount of carbon black added (ratio to magnetic particles) (part by weight)
Example 83	Example 47	5.0:1	0.50
Example 84	Example 48	5.0:1	0.50
Example 85	Example 49	5.0:1	0.50
Example 86	Example 50	5.0:1	0.50
Example 87	Example 51	5.0:1	0.50
Example 88	Example 52	5.0:1	0.50
Example 89	Example 53	5.0:1	0.50
Example 90	Example 54	5.0:1	0.50
Example 91	Example 55	5.0:1	0.50
Example 92	Example 56	5.0:1	0.50
Example 93	Example 47	5.0:1	0.00
Example 94	Example 49	5.0:1	2.50
Example 95	Example 51	5.0:1	1.50
Comparative Example 36	Comparative Example 27	5.0:1	0.50
Comparative Example 37	Comparative Example 28	5.0:1	0.50
Comparative Example 38	Comparative Example 29	5.0:1	0.50

Table 17 (continued)

Examples and Comparative Examples	Properties of coating composition	Properties of magnetic recording medium	
	Viscosity (cP)	Thickness of magnetic layer (μm)	Coercive force value (Oe)
Example 83	2,560	3.3	734
Example 84	3,064	3.5	897
Example 85	2,944	3.4	746
Example 86	2,560	3.3	967
Example 87	5,273	3.8	1,973
Example 88	2,688	3.5	741
Example 89	2,586	3.4	893
Example 90	2,560	3.3	751
Example 91	2,944	3.5	963
Example 92	4,352	3.8	1,961
Example 93	2,509	3.4	736
Example 94	3,046	3.5	746
Example 95	2,790	3.3	1,965
Comparative Example 36	3,149	3.3	735
Comparative Example 37	2,893	3.4	933
Comparative Example 38	3,020	3.4	942

Table 17 (continued)

Examples and Comparative Examples	Properties of magnetic recording medium		
	Br/Bm (-)	Gloss (%)	Surface roughness Ra (nm)
Example 83	0.88	175	7.3
Example 84	0.88	178	6.6
Example 85	0.89	171	7.8
Example 86	0.88	175	7.2
Example 87	0.88	228	7.6
Example 88	0.89	174	7.4
Example 89	0.89	175	7.0
Example 90	0.90	173	8.0
Example 91	0.90	172	8.2
Example 92	0.88	234	6.9
Example 93	0.89	173	7.6
Example 94	0.88	175	7.3
Example 95	0.89	230	8.3
Comparative Example 36	0.85	160	12.9
Comparative Example 37	0.85	160	13.1
Comparative Example 38	0.85	158	14.4

Table 17 (continued)

Examples and Comparative Examples	Properties of magnetic recording medium		
	Young's modulus (relative value)	Linear absorption (μm^{-1})	Surface resistivity (Ω/sq)
Example 83	136	1.48	3.6×10^8
Example 84	135	1.36	6.4×10^8
Example 85	140	1.53	6.3×10^8
Example 86	136	1.55	1.2×10^9
Example 87	136	1.50	6.0×10^8
Example 88	137	1.45	4.8×10^8
Example 89	140	1.41	5.1×10^8
Example 90	136	1.52	2.6×10^8
Example 91	140	1.50	1.8×10^9
Example 92	135	1.55	1.1×10^9
Example 93	135	1.48	1.1×10^9
Example 94	136	1.55	3.2×10^8
Example 95	135	1.50	3.1×10^8
Comparative Example 36	124	0.65	8.8×10^{11}
Comparative Example 37	124	0.91	8.9×10^{11}
Comparative Example 38	123	1.11	6.1×10^{10}

Table 18

Examples and Comparative Examples	Kind of core particles	Production of black magnetic acicular composite particles	
		Coating with fluoroalkylsilane compound	
		Additives	
		Kind	Amount added (part by weight)
Example 96	Core particles 1	Tridecafluorooctyl trimethoxysilane	1.0
Example 97	Core particles 2	Heptadecafluorodecyl trimethoxysilane	2.0
Example 98	Core particles 3	Trifluoropropyl trimethoxysilane	1.5
Example 99	Core particles 4	Tridecafluorooctyl trimethoxysilane	0.5
Example 100	Core particles 5	Heptadecafluorodecyl trimethoxysilane	5.0
Example 101	Core particles 6	Trifluoropropyl trimethoxysilane	1.0
Example 102	Core particles 7	Tridecafluorooctyl trimethoxysilane	1.5
Example 103	Core particles 8	Tridecafluorooctyl trimethoxysilane	3.0
Example 104	Core particles 9	Heptadecafluorodecyl trimethoxysilane	2.0
Example 105	Core particles 10	Tridecafluorooctyl trimethoxysilane	1.0
Comparative Example 39	Core particles 1	Tridecafluorooctyl trimethoxysilane	1.0
Comparative Example 40	Core particles 4	Tridecafluorooctyl trimethoxysilane	0.5
Comparative Example 41	Core particles 4	Tridecafluorooctyl trimethoxysilane	0.005

Table 18 (continued)

Examples and Comparative Examples	Production of black magnetic acicular composite particles		
	Coating with fluoroalkylsilane compound		
	Edge runner treatment		Coating amount (calculated as Si) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 96	60	30	0.06
Example 97	45	30	0.10
Example 98	30	45	0.19
Example 99	30	30	0.03
Example 100	30	30	0.25
Example 101	60	45	0.13
Example 102	60	30	0.09
Example 103	30	20	0.18
Example 104	60	30	0.10
Example 105	60	30	0.06
Comparative Example 39	30	20	0.06
Comparative Example 40	30	20	0.03
Comparative Example 41	30	20	3×10^{-4}

Table 18 (continued)

Examples and Comparative Examples	Production of black magnetic acicular composite particles	
	Adhesion of carbon black	
	Carbon black	
	Kind	Amount added (part by weight)
Example 96	A	10.0
Example 97	A	7.5
Example 98	B	5.0
Example 99	B	10.0
Example 100	C	15.0
Example 101	A	10.0
Example 102	A	7.5
Example 103	B	5.0
Example 104	B	3.0
Example 105	C	10.0
Comparative Example 39	-	-
Comparative Example 40	A	0.01
Comparative Example 41	B	2.0

Table 18 (continued)

Examples and Comparative Examples	Production of black magnetic acicular composite particles		
	Adhesion of carbon black		
	Edge runner treatment		Amount adhered (calculated as C) (wt. %)
	Linear load (Kg/cm)	Time (min)	
Example 96	60	30	9.09
Example 97	30	40	6.95
Example 98	60	30	4.74
Example 99	45	30	9.08
Example 100	60	20	13.01
Example 101	60	30	9.07
Example 102	60	20	6.96
Example 103	30	40	4.73
Example 104	45	20	2.90
Example 105	60	30	9.08
Comparative Example 39	-	-	-
Comparative Example 40	30	20	0.009
Comparative Example 41	30	20	1.96

Table 19

Examples and Comparative Examples	Properties of black magnetic acicular composite particles			
	Average major axis diameter (μm)	Average minor axis diameter (μm)	Aspect ratio (-)	Geometrical standard deviation value (-)
Example 96	0.276	0.0335	8.2:1	1.41
Example 97	0.212	0.0286	7.4:1	1.36
Example 98	0.290	0.0366	7.9:1	1.42
Example 99	0.152	0.0223	6.8:1	1.44
Example 100	0.131	0.0179	7.3:1	1.39
Example 101	0.280	0.0336	8.3:1	1.41
Example 102	0.212	0.0287	7.4:1	1.36
Example 103	0.291	0.0367	7.9:1	1.42
Example 104	0.153	0.0224	6.8:1	1.43
Example 105	0.129	0.0180	7.2:1	1.40
Comparative Example 39	0.275	0.0335	8.2:1	1.40
Comparative Example 40	0.152	0.0222	6.8:1	-
Comparative Example 41	0.152	0.0221	6.9:1	-

Table 19 (continued)

Examples and Comparative Examples	Properties of black magnetic acicular composite particles		
	BET specific surface area value (m ² /g)	Coercive force value (Oe)	Saturation magnetization value (emu/g)
Example 96	35.9	683	74.1
Example 97	40.1	832	76.3
Example 98	32.1	700	80.3
Example 99	50.8	915	78.8
Example 100	56.7	1,900	131.9
Example 101	35.6	673	73.2
Example 102	43.8	821	76.6
Example 103	32.9	691	76.8
Example 104	53.3	883	76.8
Example 105	52.6	1,891	127.5
Comparative Example 39	38.8	681	76.4
Comparative Example 40	52.2	896	81.3
Comparative Example 41	62.3	902	81.3

Table 19 (continued)

Examples and Comparative Examples	Properties of black magnetic acicular composite particles		
	Volume resistivity ($\Omega \cdot \text{cm}$)	Blackness (L^* value) (-)	Carbon black desorption percentage (%)
Example 96	5.1×10^4	18.4	6.1
Example 97	3.1×10^5	19.5	6.8
Example 98	2.6×10^5	18.9	7.3
Example 99	3.8×10^5	19.3	8.5
Example 100	5.1×10^5	18.3	7.3
Example 101	2.1×10^4	19.2	4.6
Example 102	8.3×10^4	19.1	3.6
Example 103	6.5×10^5	18.3	2.1
Example 104	1.1×10^5	18.5	3.1
Example 105	1.4×10^5	18.3	4.6
Comparative Example 39	6.9×10^8	24.5	-
Comparative Example 40	5.4×10^7	24.3	-
Comparative Example 41	1.6×10^7	23.1	48.3

Table 20

Examples and Comparative Examples	Production of magnetic coating composition		
	Kind of magnetic acicular particles	Weight ratio of particles to resin (-)	Amount of carbon black added (ratio to magnetic particles) (part by weight)
Example 106	Example 96	5.0:1	0.50
Example 107	Example 97	5.0:1	0.50
Example 108	Example 98	5.0:1	0.50
Example 109	Example 99	5.0:1	0.50
Example 110	Example 100	5.0:1	0.50
Example 111	Example 101	5.0:1	0.50
Example 112	Example 102	5.0:1	0.50
Example 113	Example 103	5.0:1	0.50
Example 114	Example 104	5.0:1	0.50
Example 115	Example 105	5.0:1	0.50
Example 116	Example 96	5.0:1	0.00
Example 117	Example 98	5.0:1	2.50
Example 118	Example 100	5.0:1	1.50
Comparative Example 42	Comparative Example 39	5.0:1	0.50
Comparative Example 43	Comparative Example 40	5.0:1	0.50
Comparative Example 44	Comparative Example 41	5.0:1	0.50

Table 20 (continued)

Examples and Comparative Examples	Properties of coating composition	Properties of magnetic recording medium	
	Viscosity (cP)	Thickness of magnetic layer (μm)	Coercive force value (Oe)
Example 106	2,714	3.5	736
Example 107	2,970	3.3	899
Example 108	2,202	3.5	743
Example 109	2,586	3.3	970
Example 110	6,040	3.8	1,975
Example 111	3,064	3.5	743
Example 112	3,149	3.4	895
Example 113	2,560	3.4	753
Example 114	2,893	3.5	965
Example 115	5,094	3.7	1,963
Example 116	2,560	3.2	738
Example 117	3,046	3.5	741
Example 118	3,149	3.4	1,963
Comparative Example 42	3,064	3.5	735
Comparative Example 43	3,200	3.4	931
Comparative Example 44	3,072	3.5	940

Table 20 (continued)

Examples and Comparative Examples	Properties of magnetic recording medium		
	Br/Bm (-)	Gloss (%)	Surface roughness Ra (nm)
Example 106	0.88	173	7.0
Example 107	0.88	173	7.0
Example 108	0.88	170	7.8
Example 109	0.89	176	6.9
Example 110	0.88	231	7.3
Example 111	0.89	170	8.1
Example 112	0.89	175	7.2
Example 113	0.89	172	7.5
Example 114	0.89	173	7.2
Example 115	0.89	233	7.1
Example 116	0.89	174	6.9
Example 117	0.88	170	7.6
Example 118	0.89	230	7.5
Comparative Example 42	0.85	161	13.1
Comparative Example 43	0.84	163	12.8
Comparative Example 44	0.85	155	14.6

Table 20 (continued)

Examples and Comparative Examples	Properties of magnetic recording medium		
	Young's modulus (relative value)	Linear absorption (μm^{-1})	Surface resistivity (Ω/sq)
Example 106	135	1.49	1.6×10^8
Example 107	136	1.41	3.8×10^8
Example 108	139	1.52	6.4×10^8
Example 109	137	1.52	1.3×10^9
Example 110	135	1.51	6.5×10^8
Example 111	138	1.46	7.2×10^8
Example 112	141	1.43	9.2×10^8
Example 113	136	1.53	2.6×10^8
Example 114	139	1.51	1.1×10^9
Example 115	136	1.55	1.3×10^9
Example 116	136	1.61	1.2×10^9
Example 117	135	1.63	4.6×10^8
Example 118	135	1.59	6.3×10^8
Comparative Example 42	122	0.63	8.1×10^{11}
Comparative Example 43	123	0.89	8.3×10^{11}
Comparative Example 44	123	1.12	7.6×10^{10}

Claims

1. A magnetic recording medium comprising:

(a) a non-magnetic base film; and

(b) a magnetic recording layer comprising a binder resin and black magnetic acicular composite particles which have an average particle diameter of 0.051 to 0.72 μm and which comprise:

- magnetic acicular particles,
- a coating on the surface of said magnetic acicular particles, comprising at least one organosilicon compound selected from:
 - (1) organosilane compounds obtainable by drying or heat-treating alkoxysilane compounds,
 - (2) polysiloxanes or modified polysiloxanes, and
 - (3) fluoroalkyl organosilane compounds obtainable by drying or heat-treating fluoroalkylsilane compounds, and
- from 0.5 to 10 parts by weight, per 100 parts by weight of said magnetic acicular particles, of carbon black particles which have a particle size of 0.002 to 0.05 μm and which are adhered to said coating.

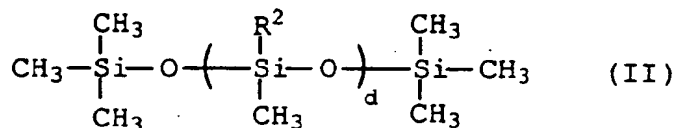
2. A medium according to claim 1, wherein said alkoxysilane compound is represented by the general formula (I):



wherein R^1 is C_6H_5 -, $(\text{CH}_3)_2\text{CHCH}_2$ - or $n\text{-C}_b\text{H}_{2b+1}$ - (wherein b is an integer of 1 to 18); X is CH_3O - or $\text{C}_2\text{H}_5\text{O}$ -; and a is an integer of 0 to 3.

3. A medium according to claim 2, wherein said alkoxysilane compound is methyl triethoxysilane, dimethyl diethoxysilane, tetraethoxysilane, phenyl triethoxysilane, diphenyl diethoxysilane, methyl trimethoxysilane, dimethyl dimethoxysilane, tetramethoxysilane, phenyl trimethoxysilane, diphenyl dimethoxysilane, isobutyl trimethoxysilane or decyl trimethoxysilane.

4. A magnetic recording medium according to any one of the preceding claims, wherein said polysiloxanes are represented by the general formula (II):



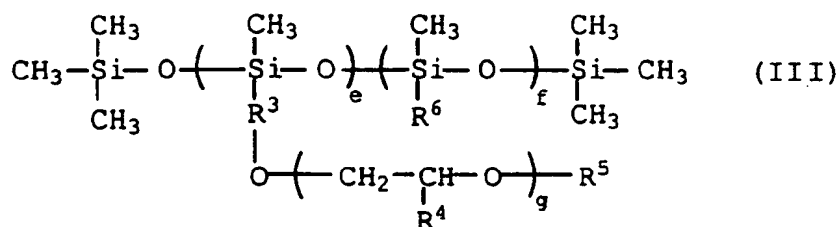
wherein R^2 is H - or CH_3 -, and d is an integer of from 15 to 450.

5. A medium according to claim 4, wherein said polysiloxanes are ones having methyl hydrogen siloxane units.

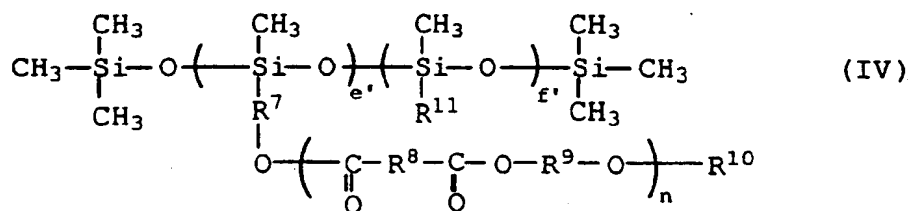
6. A medium according to any one of the preceding claims, wherein said modified polysiloxanes are selected from:

- (A) polysiloxanes modified with at least one polyether and/or polyester and/or epoxy compound, and
- (B) polysiloxanes whose molecular terminal is modified with at least one group selected from carboxylic acid, alcohol and hydroxyl groups.

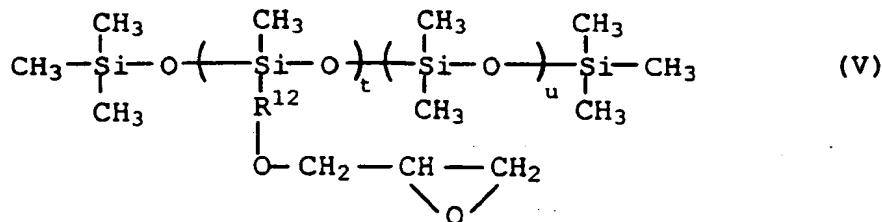
7. A medium according to claim 6, wherein said polysiloxanes (A) are represented by the general formula (III), (IV) or (V):



wherein R^3 is $-(\text{CH}_2)_h-$; R^4 is $-(\text{CH}_2)_i-\text{CH}_3$; R^5 is $-\text{OH}$, $-\text{COOH}$, $-\text{CH}=\text{CH}_2$, $-\text{C}(\text{CH}_3)=\text{CH}_2$ or $-(\text{CH}_2)_j-\text{CH}_3$; R^6 is $-(\text{CH}_2)_k-\text{CH}_3$; g and h are each independently an integer of from 1 to 15; i , j and k are each independently an integer of from 0 to 15; e is an integer of from 1 to 50; and f is an integer of from 1 to 300;

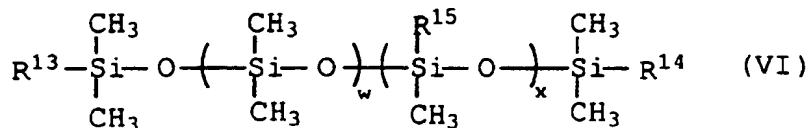


wherein R^7 , R^8 and R^9 are $-(\text{CH}_2)_q-$ and may be the same or different; R^{10} is $-\text{OH}$, $-\text{COOH}$, $-\text{CH}=\text{CH}_2$, $-\text{C}(\text{CH}_3)=\text{CH}_2$ or $-(\text{CH}_2)_r-\text{CH}_3$; R^{11} is $-(\text{CH}_2)_s-\text{CH}_3$; n and q are each independently an integer of from 1 to 15; r and s are each independently an integer of from 0 to 15; e' is an integer of from 1 to 50; and f' is an integer of from 1 to 300; or



wherein R^{12} is $-(\text{CH}_2)_v-$; v is an integer of from 1 to 15; t is an integer of from 1 to 50; and u is an integer of from 1 to 300.

8. A medium according to claim 6 or 7, wherein said polysiloxanes (B) are represented by the general formula (VI):



wherein R¹³ and R¹⁴ are -OH, R¹⁶OH or R¹⁷COOH and may be the same or different; R¹⁵ is -CH₃ or -C₆H₅; R¹⁶ and R¹⁷ are -(CH₂)_y-; y is an integer of from 1 to 15; w is an integer of from 1 to 200; and x is an integer of from 0 to 100.

9. A medium according to any one of the preceding claims, wherein said fluoroalkylsilane compounds are represented by the general formula (VII):



wherein R¹⁸ is CH₃-, C₂H₅-, CH₃O- or C₂H₅O-; X is CH₃O- or C₂H₅O-; and z is an integer of from 0 to 15; and a' is an integer of from 0 to 3.

10. A medium according to any one of the preceding claims, wherein the amount of said coating organosilicon compounds is from 0.02 to 5.0 % by weight, calculated as Si, based on the total weight of the organosilicon compounds and said magnetic acicular particles.

11. A medium according to any one of the preceding claims, wherein said magnetic acicular particles are particles having a coat on at least a part of the surface thereof and which coat comprises at least one hydroxide or oxide selected from hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon in an amount of from 0.01 to 20 % by weight, calculated as Al and/or SiO₂, based on the total weight of the coated magnetic acicular particles.

12. A medium according to any one of the preceding claims, wherein said black magnetic acicular composite particles have one or more properties selected from

- (a) an aspect ratio (average major axis diameter/average minor axis diameter) of from 2:1 to 20:1;
- (b) a BET specific surface area value of from 16 to 160 m²/g;
- (c) a blackness (L* value) of from 15 to 23;
- (d) a volume resistivity of not more than 1.0 x 10⁷ Ω·cm; and
- (e) a geometrical standard deviation of major axis diameter of from 1.01 to 2.0.

13. A medium according to any one of the preceding claims, which has one or more properties selected from

- (a) a coercive force of from 19.9 to 279 KA/m (250 to 3500 Oe) and a squareness (residual magnetic flux density Br/saturation magnetic flux density Bm) of from 0.85 to 0.95;
- (b) a gloss of from 150 to 300 %, a surface roughness Ra of not more than 12.0 nm, and a linear absorption coefficient of coating film of from 1.30 to 10.0 μm⁻¹; and
- (c) a surface resistivity of not more than 1.0 x 10¹⁰ Q/sq.

14. A method of forming a magnetic recording medium which comprises applying a magnetic coating composition comprising the black magnetic acicular composite particles as defined in any one of claims 1 to 12, a binder resin and a solvent to a non-magnetic base film, followed by drying.

15. Use of black magnetic acicular composite particles as defined in any one of claims 1 to 12 in a magnetic recording medium.

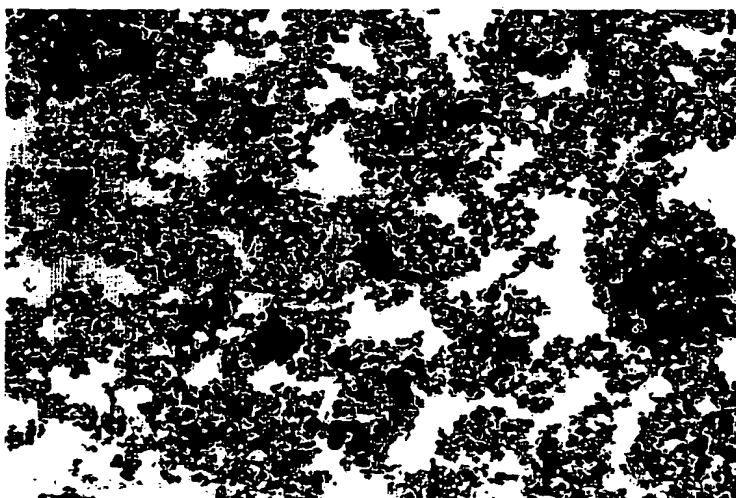
16. Black magnetic acicular composite particles suitable for use in a magnetic recording medium, wherein said particles are as defined in any one of claims 1 to 12.

FIG.1



($\times 30000$)

FIG.2



($\times 30000$)

FIG.3



($\times 30000$)

FIG.4



($\times 30000$)

FIG.5



($\times 30000$)

FIG.6



($\times 30000$)

FIG.7



(× 30000)



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 99 30 3761

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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 20 September 1999	Examiner Heywood, C
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